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THE APPLICATION TO ARTILLERY OF THE PHOTOELECTRIC CELL METHOD OF MEASUREMENT OF PROJECTILE VELOCITIES[1]

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Abstract

An outline of the method in which the projectile interrupts successively beams of light shining on photoelectric cells placed along the trajectory is given. The velocity is measured by means of records taken of the times between interruptions of the beams of light. An area about 24 by 30 in. is made sensitive to the projectile by reflecting a beam of light across this area several times, then directing it on the photoelectric cell. The details of the apparatus are given.

The recording apparatus consists of an amplifier which impresses the current pulse from the photoelectric cell on the grid of a thyratron when the projectile interrupts the light beam. This thyratron, on discharging a condenser, emits a short flash of light which is recorded on a rotating drum camera. A similar thyratron controlled by a tuning fork puts a simultaneous time record on the film. The camera is so designed that the film can be taken out and developed in daylight.

The results of firing tests in Petawawa indicate that the apparatus can be used successfully in daylight with field guns. The present equipment measures velocities with a probable error of less than 2 ft. per sec. for muzzle velocities of the order of 1600 ft. per sec. Improvements in design are discussed.

Introduction

The method of measuring the velocity of projectiles which was developed recently in the National Research Laboratories, Ottawa, has been applied to artillery and was tried suc............ .... field gun. The method is described in detail elsewhere (1 ... to rifle bullets, and is outlined briefly as follows. The ... successively beams of light shining on photoelectric ... in the photoelectric cell caused by the interruption (the projectile, after suitable amplification, is recorded photographically. An time record is also imposed on the photographic record, so that the time of flight of the projectile between successive beams of light can be measured and hence its velocity calculated.

For the present experiments a considerable part of the equipment was redesigned to make it semiportable. Some alterations were made necessary by the fact that it had to be used at a firing point unequipped with electric power. Hence much of the apparatus will be described in detail so that continued reference to previous reports will not be necessary.

Lamp and Photoelectric Cell Frames

Experience with rifle bullets indicated that good results should be obtained, in the case of a field gun, with the beams of light about 20 ft. or more apart. Actually, as the results will show, one of the greatest sources of error is in the measurement of the distance between the beams of light, because of the difficulty in locating the edge or centre of a beam of light that is not sharply defined. Obviously, greater distances apart lead to greater accuracy and ease of measurement, but practical considerations led to the choice of a distance of about 50 ft. between the light beams. Four photoelectric cell and lamp stations were used. These will be numbered Stations 1, 2, 3, and 4. Station 1 was situated about 65 ft. from the muzzle, and the others were at intervals of approximately 50 ft. along the trajectory. Only three sets of photoelectric cell and lamp equipment were constructed, so that only three of the four stations could be used at once.

Consideration of jump, errors in laying, etc., made it advisable to construct the lamp and photoelectric cell equipment in such a manner that a rectangular area about 24 by 30 in. at right angles to the trajectory would be sensitive for recording purposes. This was done by reflecting a beam of light back and forth several times between tw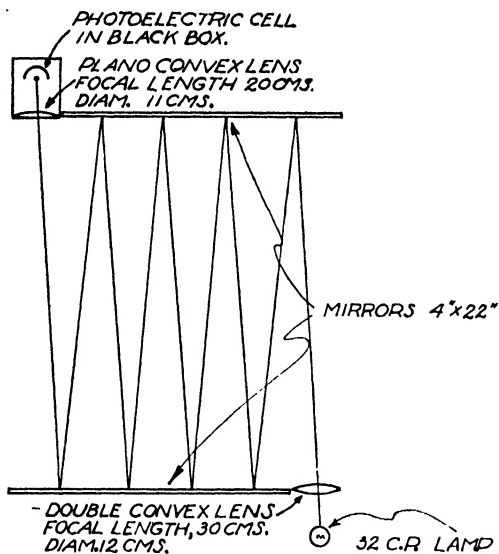o mirrors, as shown in Fig. 1. The beams of light were about four inches in diameter, and were reflected back and forth in such a manner that there were no blind areas in a central rectangular region of approximately 24 by 30 in. The mirrors, the lamp and the photoelectric cell boxes were supported on light but rigid angle iron frames whose outside dimensions were 4 by $2\frac{3}{4}$ ft.

The projector consisted of a 32 c.p., six-volt automobile headlight bulb and a single condensing lens having a focal length of about 30 cm. and a diameter of 12 cm. This simple arrangement did not give as well defined a beam of light as might be desired. However, as the present experiments were only of a preliminary nature to test the practicability of the equipment for field guns, it was not considered advisable, at present, to make further refinements on the optical system to improve the light beams. In a permanent set-up a more elaborate optical system could be designed that would give a narrower and sharply defined light beam so that its position could be located with precision.

FIG. 1. *Arrangement of light beam.*

The lamp and mirror supports were made adjustable to facilitate focusing. The lamp was housed in a box to keep stray light from the mirrors, and the photoelectric cell was housed in a reasonably light-tight box painted black on the inside. No other precautions were taken to keep daylight from the photo-electric cell, as the lens was such that very little light except from the mirror could reach the sensitive part of the cell. The cell box was placed on the top end of the frame with the lens downward so that any stray light entering it would be only that scattered from the ground. Stray light, that did not change suddenly and was not so intense that it affected the sensitivity of the photoelectric cell, would be expected not to affect the recording equipment, because only short-period pulses in the photoelectric cell current were amplified, and a steady or slowly varying small current in the cell circuit caused by stray light would not affect the recording circuit. Actually the photoelectric current caused by stray light and insulation leakage was often of the same magnitude as the current due to the light from the lamp, but though the apparatus was used both in bright sunlight and under cloudy conditions, and with clouds moving over the sun, no trouble was experienced by the effects of these stray currents.

To allow for photoelectric cells of different sensitivities and for different efficiencies of the lamp, the lamps were controlled by individual rheostats and the current adjusted so that approximately the same photoelectric current flowed in each. General Electric PJ-22 photoelectric cells were used with a series coupling resistance of one megohm and 90 volts on the anode. The light intensity employed was such that approximately 2 microamperes flowed in each cell.

Recording Apparatus

Method of Recording

In previous experiments (1, 2), three general methods of recording were used. In the first method, the photoelectric cell current, after amplification with a d-c. amplifier, was measured by means of an Einthoven galvanometer and recorded photographically. This method was discarded immediately because the arrangement was too sensitive to disturbances, and the Einthoven galvanometer had too long a natural period. In the second method, the amplified pulse of the current produced when the projectile interrupted the beam of light was impressed on the grid or control electrode of a thyratron in such a way that the thyratron discharged a condenser; the discharging current was recorded by the Einthoven galvanometer. An a-c. amplifier was used in this case. This method gave satisfactory results, but was improved considerably in the third experiment in which the Einthoven galvanometer was eliminated, and a photographic record was made of the flash of light emitted by the thyratron when it discharged a condenser. Another thyratron that was controlled by an electrically driven tuning fork and that emitted either 500 or 1000 flashes per second produced the time marks on the photographic film.

Fig. 2 shows a schematic arrangement of the new recording equipment used in the present investigation. The amplifier controls thyratron *A* in such a manner that each time a beam of light is interrupted by the projectile the thyratron discharges a condenser and emits a very short flash of light. (The
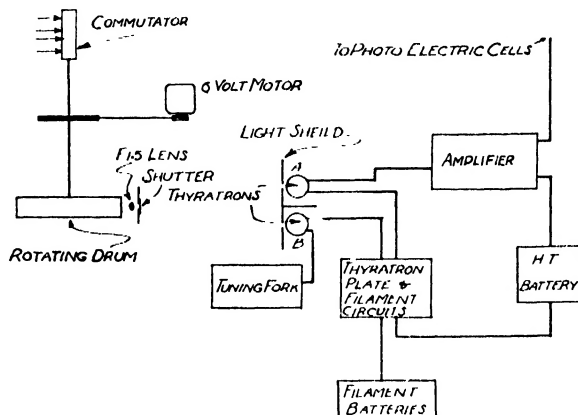

FIG. 2. *Schematic arrangement of recording equipment.*

flash lasts for only a few microseconds, probably less than five.) Thyratron *B* produced the time marks. These flashes of light are recorded on a rotating drum camera placed in front of the thyratrons as shown. A narrow slit directly in front of the camera defines the beam of light, and the lens forms an image of this slit on the film. A commutator driven on the same axis as the camera controls the time at which the gun is fired and the time at which the camera shutter is opened; both operations are done electrically.

The Camera

The design of the new camera incorporated several improvements over that used with rifle bullets. The film (motion picture) was carried on a drum about 10 in. in diameter which rotated at the required speed and was driven by a six-volt d-c. motor. A diagram demonstrating the essential features is shown in Fig. 3. The camera was so designed that the whole process of taking the records, developing them, etc., could be carried out in daylight; the only process that required a dark room was the loading of the film spool. This spool carried about 125 ft. of film or enough for about 40 rounds. The film spool was light-tight so it could be mounted in the camera in daylight. Hence, by duplicating film spools, the apparatus could be used indefinitely without recourse to a dark room.

When in operation the film spool was carried inside the rotating drum and coaxial with it. The film was fed from the spool through a set of driving sprockets around the drum and over another driving sprocket, so that it could be wound off the drum through a narrow slit in the back of the camera. This slit opened into a dark box containing the developing tank, etc. To take an exposed record off the drum and to reload the camera, the rotating

drum was clamped, the gears attached to a crank were engaged with the gears driving the film sprockets, and the length of exposed film was wound off the drum into the dark box at the back of the camera. The film was then cut off with a knife that was attached to the slit, and the camera was ready for another exposure.
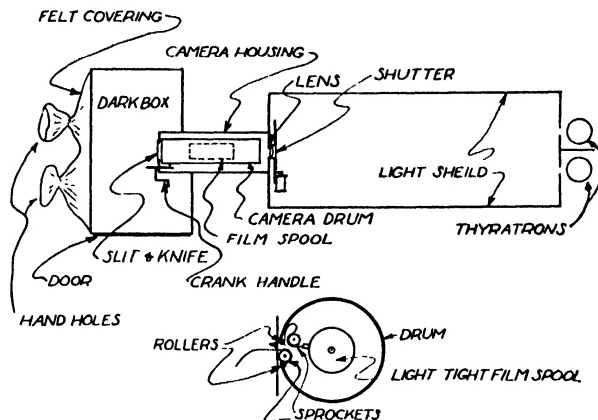

FIG. 3. *Schematic diagram showing essential features of camera.*

The part of the camera carrying the slit, knife and gears, was hinged so that it could be moved back from the drum to clear the gears, etc. The knife acted as a cover for the slit so that the dark box could be opened and the developing tank could be removed or inserted without causing fogging of the film on the drum. The loading of the exposed film into the developing tank was done by hand in the dark box. The hands were inserted through sleeve holes in the back of the box. The developing solution was not, as a rule, poured into the tank until the film was inserted and the tank removed from the dark box. The process of preparing the camera for another exposure and placing the film in the tank ready for development could be carried out in two minutes or less, so that with the present apparatus firing could be carried on at approximately that interval. To develop, fix and wash the film in such a way that a rough estimate of the velocity, say to about 20 ft. per sec., could be obtained, required about 15 min. For accurate measurement, a traveling microscope or an equivalent instrument must be used.

During the course of the tests at Petawawa, no dark room was used at all as sufficient film was wound on one spool for the tests, and development, etc., was carried on in daylight, sometimes almost in direct sunlight.

The apparatus could, of course, be made much more automatic. In fact, before it was built, preliminary designs were made of a much more elaborate camera in which the exposed film was automatically wound into a developing tank containing developer; then the film was washed and fixed, and it emerged from the apparatus ready for drying and measurement. If the velocity measurements were not required immediately, the exposed films could be marked and stored in the dark box and developed after the shooting was over.

The developing tank, made of Monel metal had a removable lid and contained a flat bakelite spool. Spiral grooves were cut in the end plates of the spool so the film could be fed into these grooves and so held by its edges that its surfaces were not in contact. A pouring funnel and air vent, both made light-tight, made it possible to pour the chemicals in and out of the tank in daylight.

The lens used on the camera was a Dalmeyer F 1.5 with a focal length of one inch. This lens produced on the film an image of the slit in front of the thyratrons. In the apparatus used with rifle bullets a cylindrical lens was used which focused a line image of the slit in front of the thyratron. The record made with the Dalmeyer lens was much sharper and led to easier reading of the record with the microscope. Since the record consists of short lines with sharp edges fading to nothing at their ends instead of uniform lines as in the records obtained by the previous apparatus, they are not so easily reproducible and cannot be examined so readily by the eye. The lens used in the present experiment had more light-gathering power than the cylindrical lens used previously. The slit in the shield in front of the thyratrons was about $\frac{1}{4}$ in. wide and was placed 30 in. from the lens, so that the spots on the record were approximately 1/120 in. wide and about 1/32 to 3/64 in. long.

The shutter consisted of a rotating sector placed in front of the lens. To open and close the aperture, the sector was so designed that it rotated through about two-thirds of a revolution. The sector was driven by a spring, and the time of exposure was controlled by air damping in a dashpot. The piston was connected to the sector by a crank arm so that the motion of the sector during opening and closing would be very rapid, the control being exerted around the centre of the stroke while the shutter was open. The shutter was released electromagnetically and controlled by the commutator indicated in Fig. 2.

Amplifier, Photoelectric Cell, Thyratron and Tuning Fork Circuits

The amplifier was of the resistance capacity coupled type having a high gain. A rough measure of the gain gave a maximum voltage ratio of about 10,000, the circuit being designed for voltage amplification only, not for power output. The circuit diagram is shown in Fig. 4. The only feature worth special note in this circuit is that all the tubes were carefully decoupled from the high tension batteries with 25,000-ohm resistances and two microfarads condensers as shown. The reason for special care in decoupling was that the batteries which fed the amplifier were also used to feed the thyratron plates, and when the thyratron discharges the condenser producing the flash of light for the record, sudden loads are put on the battery which would react on the amplifier unless care were taken in decoupling. The thyratron plate circuits were decoupled from the battery as will be described later. The photoelectric cells were connected to the amplifier as shown, so that a sudden decrease in photoelectric cell current caused a positive voltage pulse on the grid. Actually only about one-quarter of the gain of the amplifier was needed. If the gain was set too high, the apparatus was subject to inter-

ference which will be discussed later; if set too low one or more of the stations might fail to produce a record. The choice of the input condenser (0.001 mfd., Fig. 4) is important in this apparatus. In the apparatus used with rifles in the basement of the National Research Laboratory in Ottawa, a
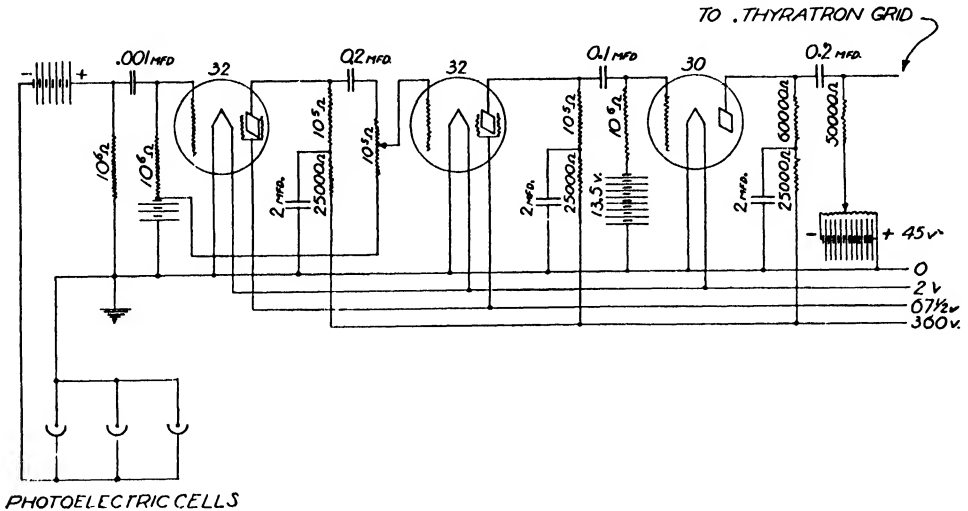

FIG. 4. *Circuit diagram of amplifier.*

considerable amount of trouble was experienced owing largely to vibrations in the lamp and photoelectric cell frames caused by the muzzle blast. A great deal of this was eliminated by choosing an input condenser so small in capacity that the low frequency pulses did not pass the condenser, while the short pulse caused by the bullet would be transmitted to the grid of the first tube with negligible attentuation. In the present case a condenser of 0.001 mfd. was chosen as about the smallest practicable capacity.

When the apparatus was first set up at Petawawa considerable interference was experienced which is believed to be due to atmospherics. The wires connecting the amplifier with the photoelectric cells were hung overhead on trees and posts. As local thunderstorms were numerous and the amplifier is very sensitive, it was not entirely unexpected that some atmospherics should be picked up. However, this trouble was eliminated by burying the wires underground or pegging them down to the surface of the ground.

Fig. 5 shows a circuit diagram for the plates and filament circuits of the thyratrons. The filaments, requiring 2.5 volts each, were connected in series for the sake of convenience so that they could be fed from a six-volt battery. To compensate for slight differences in the filament resistances a small rheostat not shown in the figure was connected across the filament of higher resistance, so that the required 2.5 volts could be kept correct across both filaments. A jack (not shown) for a voltmeter to check the voltage completes the filament circuit. The plate circuit was decoupled from the batteries as shown. When the positive pulse from the tuning fork or amplifier is impressed on the grids,

the 0.5 mfd. condensers discharge through the thyratron concerned and the condenser starts to recharge immediately through the resistance A, the drop in it being sufficient to extinguish the arc in the thyratron. The decoupling condensers and resistance (5 mfd. and 1,000 ohms) smooth out the battery current required to recharge the condenser, so there is no effective reaction on the amplifier fed from the same battery.
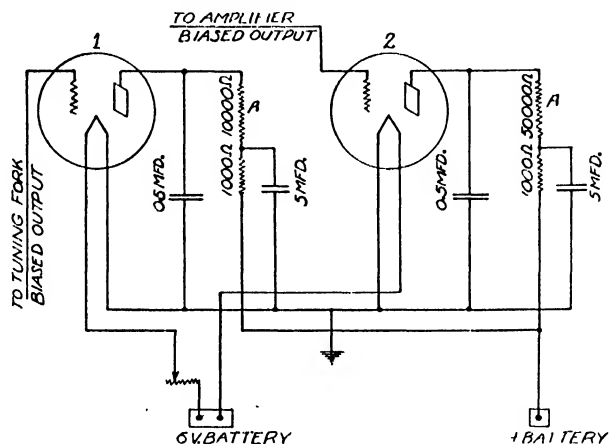

FIG. 5. *Circuit diagram for the thyratrons. 1. Time marker controlled by tuning fork. 2. Controlled by photo electric cells.*

Thyratrons of a commercial type, namely, General Electric FG-17, were used with this equipment. Unfortunately, the General Electric Company has changed some structural details of this tube recently, making it unsuitable for this type of recording. The control electrode in the older type which was used here consisted of a cylinder made from perforated sheet metal so that considerable light was emitted. In the new type the control electrode is constructed from plain sheet metal, the result being that except for that from a small hole virtually no light is emitted. This small hole would give sufficient light for a good readable record if less reduction in the size of its image on the film were used, but would not be as satisfactory as the slit used in the present arrangement. However, the FG-17 is not the only tube having suitable electrical characteristics. A more suitable tube has been built specially for the purpose by the writer (3), but as it is not a commercial product, it was not used. There are other commercial tubes that would work very well; for instance, an open type rectifier tube might be used in series with a thyratron. This has the disadvantage that extra insulated filament batteries would be required. Probably the most suitable commercial tube would be one similar to that used with the Westinghouse Strologlow equipment No. KU-610, though this has not been tried, nor have the possibilities of other commercial products been investigated. There is, however, not the slightest doubt that a commercial tube as efficient as the FG-17 for the required purpose could be found easily, and it has been shown definitely that very satisfactory tubes can be constructed.

The tuning fork equipment was of a standard type manufactured by the Cambridge Instrument Company. It consisted of a 1,000-cycle steel tuning fork maintained in vibration electromagnetically by a circuit involving a vacuum tube, so that no mechanical contacts are required on the vibrating fork. The circuit details are not given as it is a standard manufactured product. The circuit includes an output transformer in order that an alternating voltage of about two volts may be obtained from the fork. An impedance matching transformer with tapped secondary was inserted in the circuit so that a slightly higher voltage could be impressed on the grid of the thyratron. The tuning fork, a 45-volt biasing battery and a potentiometer were enclosed in a metal box in order that the electric fields generated in the tuning fork circuit would be shielded from the amplifier.

The tuning fork was calibrated some time before it was used in Petawawa, and a recalibration was made shortly after it was returned to Ottawa. Its frequency was found to be 995.9 ± 0.1 cycles per second. The calibration was made by comparing it with the radio frequency standards belonging to the Canadian Broadcasting Corporation. The accuracy of these standards is known to one part in ten million.

Commutator and Firing Circuits

As was mentioned previously, it was essential that the firing of the gun and the tripping of the shutter take place in proper sequence so that the record would appear in the correct place on the film. To ensure this an electrically controlled mechanical firing mechanism was built, which will be described in the next paragraphs. The position of the contacts on the commutator had to be adjusted ahead of the actual time of the beginning of the exposure to compensate, for the lag in the shutter, for the time taken for the firing mechanism to fire the gun, and for the time taken for the shell to approach the first photoelectric cell station. The lag in the shutter was easy to adjust experimentally by running the camera at the correct speed, taking exposures, making adjustments on the commutator and shutting the dashpot until the record appeared in the correct position on the film. Once the shutter adjustments on the commutator and dashpot were made they did not have to be reset unless wide variations in camera speed were used. The time between the firing of the gun and the shell reaching the first station could be calculated with sufficient accuracy, for the purpose, from the approximate velocity of the projectile and the known distances involved, but the time lag in the firing mechanism had to be measured. This was done by inserting an insulated electrical contact in place of the cap in a used cartridge, and using the contact made on this by the firing pin to control the thyratron which would normally be controlled by the photoelectric cells. The gun time lag was found to be much greater than the shutter time lag, hence the firing contacts on the commutator had to be made first. The correct time lags were set on the commutator before the apparatus was shipped to Petawawa, and when the actual firing was carried out it was found that no further adjustment was necessary as the first records appeared on the correct

portion of the film. On the last day of firing when the distances of the photo-electric cell stations were increased beyond that for which the original time lags were calculated, the gun firing contacts were set slightly forward though the position of the record on the film was such that this was not necessary.

The electrical circuit controlling the shutter and firing mechanism is shown in Fig. 6. In operating the apparatus, the operator has no way of knowing whether he closes the switch before the firing contacts close or between the
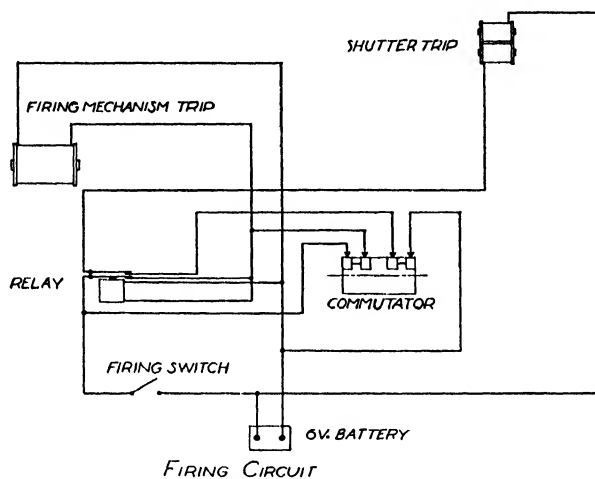

FIG. 6.   *Circuit diagram for electrically controlled shutter and firing mechanism.*

times at which the gun contacts and the shutter contacts are closed. If it should be the latter case the shutter would be tripped and the exposure made before the gun was fired, so no record would be obtained. In order to avoid this, some auxiliary equipment had to be introduced to prevent the shutter from operating until after the firing circuit was completed. This was done by introducing into the circuit a relay whose winding was in parallel with the firing trip coil. The relay has two separate contacts on its armature, one of which is merely a holding circuit, so it will stay closed, once it is energized, during the time that the firing switch is closed, and the other contact controls the battery power on the shutter coil and shutter contacts on the commutator.

Firing Mechanism

In order to avoid the necessity of any alterations to the usual firing mechanism on the gun, it was decided that the electrically controlled auxiliary firing mechanism should be so constructed that it would pull the firing handle in the usual way. Further, such a firing mechanism could be adapted easily to fire other types of guns in common use. Hence, a spring driven mechanical firing mechanism was designed which could be released electrically and which would exert enough pressure to fire the gun easily. A schematic diagram of the arrangement of the various links used to transmit the spring tension to the firing handle is shown in Fig. 7. To apply a straight spring directly to

the firing handle would have necessitated the use of a very long spring. Further, the maximum force is required near the end of the stroke rather than at the beginning. Hence the arrangement of the spring and connecting links was made such that at the beginning of the stroke the mechanical advantage between the spring and the link pulling the firing handle was about 0.3, or the force applied at the beginning of the stroke was 0.3 times the spring force when the mechanism was in the fully cocked position (the schematic drawing shows it in the cocked position). On the other hand, at the end of the stroke the ratio was 1 : 1, so that the full force of the spring was exerted on the firing handle. The spring unit consisted of 12 Ford valve springs, two parallel banks of six in series. A calibration of a sample spring showed that the total
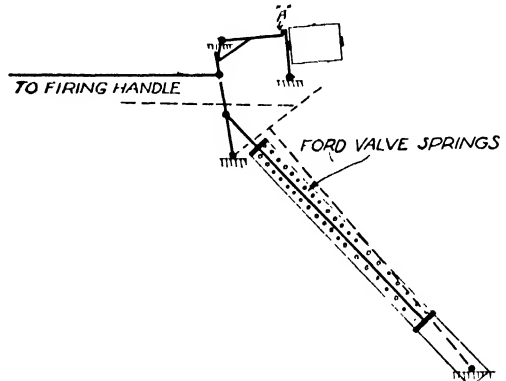

FIG. 7. *Schematic diagram showing electrically controlled firing mechanism.*

force exerted by the unit at full cock was about 164 lb., while in the uncocked position the force was about 82 lb. If friction is neglected, and the mechanical advantages mentioned above are used, this indicates that a static force in the firing handle varying from about 50 lb., at full cock, to about 82 lb. at the end of the firing stroke was available. The apparatus possessed the necessary reserve power to cock and fire the gun mechanism. The time lag between the closing of the firing circuit contacts on the commutator and the firing pin striking the cartridge was very close to $\frac{1}{10}$ sec., three separate measurements differing by not more than 6%. The magnetic trip consisted of two links as shown. The final trigger at A (Fig. 7) was a roller, so that a very small magnetic pull, probably less than an ounce, would trip the whole mechanism.

Results

Results of Firing Trials

The apparatus was taken from Ottawa to Petawawa on July 22, 1935, and was set up at a convenient range in the vicinity of the military camp. By the afternoon of July 24 various troubles, such as interference due to atmospherics, had been eliminated, and the apparatus was ready for firing. Four rounds were fired on July 24. The first round was used to verify the jump calculations by firing through paper screens instead of the lamp and photoelectric cell frames. It also served to test the firing apparatus. Jump calculations proved to be correct, so the frames were mounted in position. For Rounds 2, 3 and 4 only two lamp- and photoelectric-cell stations were used, namely, 2 and 3. The results of all firing are summarized in Table I. On the following day four more rounds were fired, using Stations 1, 2 and 3, and various settings of the gain control on the amplifier. With about 18 to 20%

of the gain of the amplifier, the record showed the three flashes of light which were identifiable as being due to the three photoelectric-cell stations, but there were also three other flashes probably due to the effect of the muzzle blast in causing the first lamp frame to vibrate. With a reduced gain, about 13%, the interference was reduced to one flash, though again a good velocity measure could be made. With the gain reduced to about 9% only one station recorded. Hence with the equipment used, the limit, between a record showing the three desired flashes with no interference and such a reduced sensitivity that no record was obtained, was too small to be practicable. In the present case the interference attributable to the muzzle blast had no detrimental effect on the actual measure of the velocity, as it does not occur at nearly the instant that the shell is passing through one of the

TABLE I

RESULTS ROUND BY ROUND

Round	Velocity in feet per sec.		
	Station 1 and 2	Station 2 and 3	Station 3 and 4
1	Trial round with paper screens.		
2		1606	
3	No record (shutter improperly set).		
4		1605	
5	1592	1586	
6	1596	1587	
7	No record (amplifier setting too insensitive).		
8		1592	
9		1609	1598
10		1595	1600
11		1610	1602
12		1596	1588
13		1606	1598
14		1593	1589
15		1589	1585
16			1590

light beams. However, with different velocities this interference might be serious. To overcome it two alternative procedures were available: First, by a change in the structure of the first lamp and photoelectric cell frame, such as increasing its rigidity and using more intense light beams, or, secondly, the use of photoelectric cell stations at greater distances from the muzzle. The first alternative was not practicable in the present case without considerable machine shop work, and as it was desirable to obtain as perfect a record as possible with little delay, the second alternative was tried. On the following day, July 26, a fourth lamp and photoelectric cell station was set up about 50 ft. beyond Station 3, and the equipment at Station 1 was moved to Station 4. With Stations 2, 3 and 4 in operation and the amplifier set at about 20% of full gain, eight rounds were fired. A good record was obtained for each round except the last, when for some unaccountable reason Station 2 failed to record.

The distances from the muzzle and between the various stations are given in Table II.

TABLE II

Measured distance	Feet
Muzzle to Station 1	66.07
Muzzle to Station 2	117.11
Station 1 to Station 2	51.04
Station 2 to Station 3	49.68
Station 3 to Station 4	52.35

In the case of Round 3 no record was obtained because of a misadjustment in cocking the camera shutter. In all other cases except Round 16 a complete record was obtained as expected, and except for Round 10 a reasonable measure of the velocity was obtained in every case. In the case of Round 10, owing perhaps to some interference occurring almost at a time when the shell was passing a light beam, an improbable result was obtained, in that the shell appeared to increase in velocity as it moved farther from the gun. The exact reason for this result remains unknown, and this round has been omitted in all further discussion. A reversed print from the record of Round 15 is shown in Fig. 8.

Accuracy

A full discussion of the sources of error with the type of apparatus used in this experiment is given in a previous paper (1). The sources of error which may affect the results are in the measurement of records and in the location of the point where the shell interrupts the beam of light. Errors in measurement of the record can be neglected, as the distances between the marks on the film could be measured to $\frac{1}{50}$ mm., which corresponds to a velocity error of about 0.3 ft. per sec. The second source of error is much more important, that is, in measuring the distance between photoelectric-cell stations. This is due to the fact that the optical system used did not define the beam of light with sufficient accuracy. The distance between stations was measured from corresponding points on the steel frames supporting the lamps, photoelectric cells and mirrors. This distance could be measured to about $\frac{1}{8}$ in. which would represent a negligible error in velocity. The optical parts at each station were made similar, but the point where the nose of the shell interrupted sufficient light to cause the thyratron to function might vary from round to round or station to station by as much as $1\frac{1}{2}$ to 2 in. owing to the fact that the beam of light was more or less circular in cross section. An error of two inches in the distance between stations represents an error in velocity of about 5 ft. per sec. As was
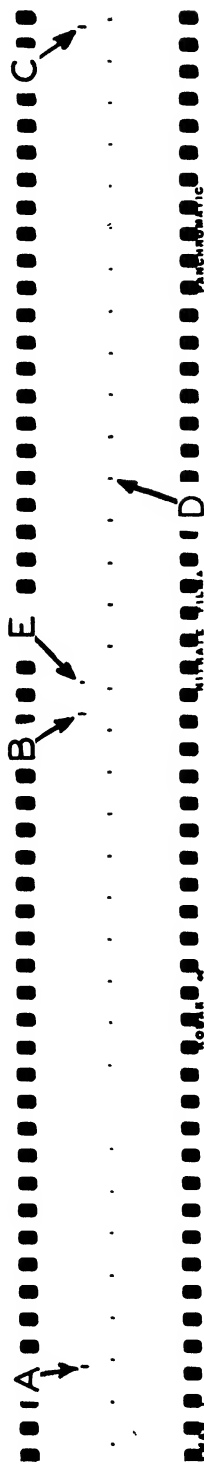

Fig. 8. *Record for Round 15. A. Station 2. B. Station 3. C. Station 4. D. Time marks, 497 9 per sec. E. This flash occurs occasionally because of the relatively long period of recovery of the amplifier after an intense pulse. It is easily recognized from the period following the previous flash which is a characteristic of the thyratron circuit. It does not affect the result.*

mentioned previously, this error could be reduced considerably by redesigning the projection apparatus. This would be comparatively easy if electric power were available at the firing point where trials were being made, as a narrow well defined beam of light could be produced by using a longer focus projecting lens and a more intense source. With the present apparatus the power had to be furnished by storage batteries, and as the apparatus had to be made portable it was necessary to limit the number of batteries carried to a minimum. Further, standard makes and easily replaceable lamps, lenses, etc., were used throughout. There is no doubt that, with a little further investigation at perhaps but slightly greater expense, new projection equipment could be constructed which would reduce the maximum error due to this uncertainty to 1 or 2 ft. per sec. for distances between stations of 50 ft. Of course, if greater distances were used the error would be proportionately lower. Actually, the mean difference between velocities in Columns 3 and 4, Table I, for the last eight rounds (except Round 10) is 7.2 ft. per sec. The mean deviation of this difference from the mean difference is 2.1 ft. per sec. Hence from these observations the probable error is of the order of 2 ft. per sec., though too few rounds have been fired for a reliable estimate.

General Conclusions

The results described in this report indicate that the photoelectric cell method for measuring projectiles is easily applicable to artillery. The equipment is not affected by daylight and the first observing station can be located as close as 100 ft. from the muzzle, for the gun used for these trials. With more rigid structures this distance could probably be made considerably shorter. The apparatus could be made portable in that it could be mounted on a truck and be ready for operation as quickly as supports for the lamp and photoelectric cell frames could be mounted. However, except in special gun positions where low trajectories of 200 ft. or so can be used, this might involve considerable structural work. Further, if electrical power were available several simplifications in design and operation could be made.

Acknowledgments

These experiments were carried out with the collaboration of Major G. P. Morrison, R.C.A., and their success is due to his enthusiasm and numerous contributions to the design and operational details. The thanks of the writer are also due to the Camp Commandant, Petawawa, for providing facilities and men to carry out the tests in Petawawa, and to the O.M.E.C.C. for structural details and for repairs made in the Ordnance workshop in Petawawa.

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NOTE ON THE ACCELERATION OF SHIPS[1]

BY K. F. TUPPER[2]

Abstract

Calculations were made of the time and distance required for a ship to accelerate to any fraction of its maximum speed, and are intended to serve as a guide in determining the length of run to be made in approaching the measured course in the conduct of ship speed trials. The effect of inaccuracy in the underlying assumptions was examined. Curves and tables are presented and offered as suitable for use.

It has frequently been noticed that when a ship is making a speed trial on a course where the halfway point is marked, the mean speed over the second half of the course is higher than that over the first half (2, p. 416). Consideration of the ship acceleration problem shows that the acceleration continuously decreases as the speed approaches its maximum value, so that on either a space or time base the speed approaches its terminal value asymptotically. Of practical interest, during the conduct of speed trials of ships, is the question of how far the ship should be run in approaching the measured course to ensure that it will have reached a sufficient fraction of its true maximum speed. As a guide in this respect, calculations based on certain approximations for the characteristics of the ship have been made for the time and distance necessary to attain any speed.

Three assumptions have been made for the variation of thrust with speed. Two of these have been chosen to give upper and lower limits so that the effect of inaccuracy in the third, which has been adopted, may be studied. Using this approximation for thrust, the variation of the ship resistance has been dealt with; this yielded expressions for time and distance required to attain any speed in terms of quantities known for any ship.

Symbols

Let v = speed of ship in feet per second,

v_m = maximum speed of ship in feet per second,

r = water resistance of ship in pounds,

r_m = water resistance of ship at maximum speed,

f = effective thrust of propeller in pounds,

x = speed fraction = $\dfrac{v}{v_m}$,

t = time in seconds,

m = mass of ship + virtual mass of surrounding water in slugs,

s = distance in feet,

n = exponent of v in expression of ship resistance.

Thrust Variation Assumptions

The acceleration of a ship depends on the variation of effective thrust with speed. In reality this is determined by the manner in which the propellers are accelerated and by the characteristics of the propellers themselves. Some simplification is necessary if a mathematical treatment is required, and to this end three arbitrary assumptions have been made for the thrust-speed relation. Fig. 1 shows curves of thrust against speed, and Fig. 2 shows the consequent power-speed relation. The assumptions that determine these curves are outlined separately as follows.
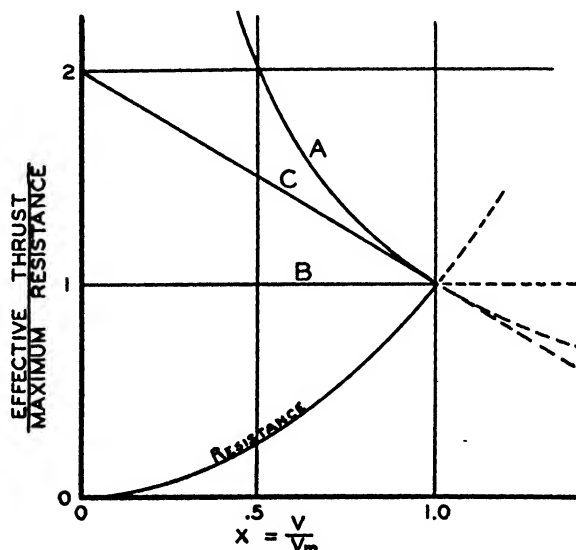

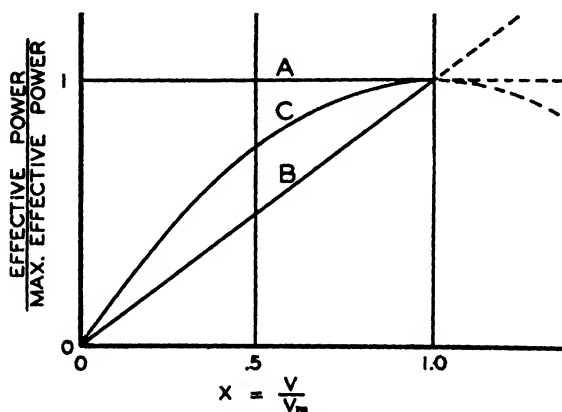FIG. 1.   *Curves showing the variations of propeller thrust with speed assumed for study.*

FIG. 2.   *Curves showing the variation of effective power associated with the assumed thrusts.*

Case A   Upper Limit of Thrust

The upper limit of thrust is given by the condition that the effective power is constant throughout,

$$fv = \text{constant} = r_m v_m \, ,$$

hence

$$f = \frac{1}{x} r_m \, .$$

The thrust varies inversely with the speed, and as a consequence rises to an infinitely high value at zero speed, a condition obviously untrue. At the high speed end of the curve the assumption of constant effective power is probably quite close to real conditions.

Case B   Lower Limit of Thrust

A lower limit for thrust has been given by the assumption of a constant thrust, independent of speed,

$$f = r_m \, .$$

It is known that for a constant rotational speed the static thrust of a propeller is in general two or three times as great as the thrust at maximum efficiency, so that the above condition may be taken as a lower limit.

An inspection of the curve of effective power for this case shows that there is a departure from real conditions at the high speed end, where the curve should have a maximum value at $x = 1$ and hence a zero slope.

Case C   Linear Thrust Relation

The assumption is made that the thrust varies linearly with speed, beginning at a certain finite value and decreasing with speed.

$$f = a - bv \, .$$

The constants a and b are related to each other by satisfying the condition for maximum effective power when $v = v_m$, and are related to r_m by the fact that $f = r_m$ at the same point.

Effective power $= fv = av - bv^2$

$$\frac{d(EP)}{dv} = a - 2bv$$

$$= 0 \quad \text{when} \quad v = v_m \, ,$$

so that

$$a = 2bv_m$$

and

$$f = (2 - x) r_m \, .$$

The static thrust is, therefore, just twice the thrust at maximum speed. This is a reasonable value, and the shapes of the thrust and consequent power curves are also reasonable.

Resistance Variation Assumption

The water resistance of a ship may be fairly well approximated by an expression of the form,

$$r = kv^n \, ,$$

since

$$r_m = kv_m{}^n \, ,$$

$$r = x^n r_m \, .$$

If such an expression for resistance be chosen, it is important in the present instance to select n so that the portion of the resistance curve in the vicinity of $x = 1$ is well approximated, since the greater portion of either space or time required for acceleration is taken up in this period when the speed is high and the acceleration is low.

The value of n must be selected from the known or calculated curve of ship resistance. For slow speed ships it is in the neighborhood of 2, but it increases to much higher values for medium and high speed ships.

The Mass to be Accelerated

Not only must the mass of the ship be accelerated but also the "virtual mass" of the surrounding water which is associated with its motion.

Theoretical work on the virtual mass of airships has shown that it is dependent upon the fineness ratio and particularly upon the shape and fineness of the ends (1, 3). The virtual mass of ship models was measured experimentally by von den Steinen (4), and the values obtained by him are sufficiently accurate for the present purpose. For the three models, a fishing boat, a freighter and a Maierform ship, the value for the virtual mass of the surrounding water was approximately 0.08 times the mass of the water displaced by the model.

For practical purposes of acceleration calculations, m may be taken as 1.08 times the mass of the ship.

The Equation of Motion and its Solution

The equation of motion for the ship is

$$m \frac{dv}{dt} = f - r . \qquad (1)$$

Changing the variable from v to x gives

$$m v_m \frac{dx}{dt} = f - r ,$$

f and r, however, are functions of x, according to the different thrust and resistance assumptions made above. Separation of the variables and integration gives the following expressions for the time,

$$\text{Case } A \qquad t = \left(\frac{m v_m}{r_m} \right) \int \frac{x\,dx}{1 - x^{n+1}} + \text{constant} ,$$

$$\text{Case } B \qquad t = \left(\frac{m v_m}{r_m} \right) \int \frac{dx}{1 - x^{n}} + \text{constant} ,$$

$$\text{Case } C \qquad t = \left(\frac{m v_m}{r_m} \right) \int \frac{dx}{2 - x - x^{n}} + \text{constant} .$$

Substitution for dt in the equation of motion,

$$x v_m = v = \frac{ds}{dt}$$

$$dt = \frac{ds}{x v_m}$$

gives

$$m v_m^2 x \frac{dx}{ds} = f - r .$$

By separation of the variables, and integration, the following equations for the distance are obtained.

$$\text{Case } A \qquad s = \left(\frac{mv_m^2}{r_m}\right)\int \frac{x^2 dx}{1-x^{n+1}} + \text{constant},$$

$$\text{Case } B \qquad s = \left(\frac{mv_m^2}{r_m}\right)\int \frac{x dx}{1-x^n} + \text{constant},$$

$$\text{Case } C \qquad s = \left(\frac{mv_m^2}{r_m}\right)\int \frac{x dx}{2-x-x^n} + \text{constant}.$$

It is seen that the general form of the expression for t is

$$t = \left(\frac{mv_m}{r_m}\right) F_T(x),$$

and for s it is

$$s = \left(\frac{mv_m^2}{r_m}\right) F_S(x),$$

where $F_T(x)$ and $F_S(x)$, which may be called the time factor and space factor, respectively, are functions of the non-dimensional speed fraction x and the exponent n. It will be noticed that the bracketed quantities, $\left(\frac{mv_m}{r_m}\right)$ and $\left(\frac{mv_m^2}{r_m}\right)$, have the dimensions of time and length, respectively, and that the use of any congruent system of units besides the foot-pound-second system suggested, is permissible.

For the comparison of the three assumptions regarding the thrust, the space and time factors can be evaluated. The integrals have been solved for certain integral values of n, and the constants of integration were determined by putting t and s each equal to zero when $x=0$. The case of $n=2$, which applies to all slow ships (where the resistance is predominantly skin friction), yields the following:

$$\text{Case } A \quad F_T(x) = \tfrac{1}{3}\left[\tfrac{1}{2} \log \frac{(1+x+x^2)}{(1-x)^2} + \sqrt{3}\ \arctan \frac{2x+1}{-\sqrt{3}} - \sqrt{3}\ \arctan \frac{-1}{\sqrt{3}}\right]$$

$$F_S(x) = -\tfrac{1}{3} \log (1-x^3),$$

$$\text{Case } B \quad F_T(x) = \tfrac{1}{2} \log \frac{(1+x)}{(1-x)}$$

$$F_S(x) = -\tfrac{1}{2} \log (1-x^2),$$

$$\text{Case } C \quad F_T(x) = \tfrac{1}{3}\left[\log \frac{(2+x)}{(1-x)} - \log 2\right]$$

$$F_S(x) = -\tfrac{1}{3}\left[\log \left\{(2+x)^2 (1-x)\right\} - \log 4\right].$$

Tables I and II of $F_T(x)$ and $F_S(x)$, respectively, for the three cases for values of x between 0.9 and 0.999, have been computed. The computed values have been plotted and are shown in Figs. 3 and 4 for direct comparison (for convenience the arbitrary base of $-\log (1-x)$ was used).

TABLE I

TIME FACTORS $F_T(x)$

x	Case A $n=2$	Case B $n=2$	Case C					
			$n=2$	$n=2.5$	$n=3$	$n=3.5$	$n=4$	$n=10$
0.900	0.52	1.47	0.89	0.83	0.78	0.75	0.72	0.62
0.950	0.76	1.83	1.13	1.03	0.96	0.91	0.87	0.70
0.980	1.06	2.30	1.44	1.30	1.20	1.12	1.06	0.79
0.990	1.29	2.64	1.67	1.50	1.39	1.28	1.21	0.86
0.995	1.52	2.99	1.90	1.70	1.55	1.43	1.35	0.93
0.997	1.69	3.25	2.07	1.84	1.68	1.55	1.42	0.97
0.999	2.06	3.80	2.44	2.16	1.95	1.79	1.67	1.07

TABLE II

SPACE FACTORS $F_S(x)$

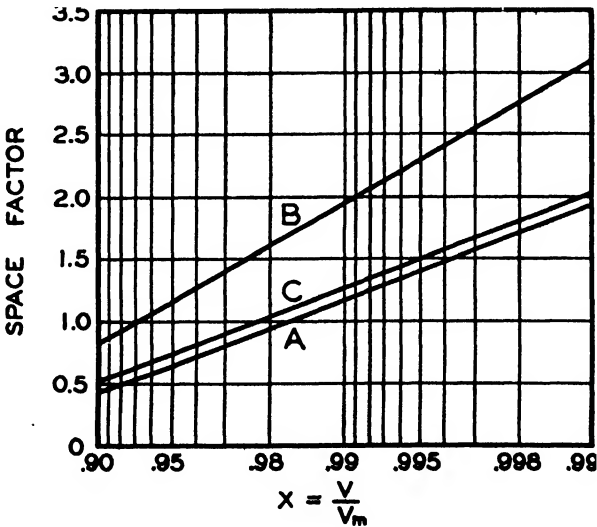| x	Case A $n=2$	Case B $n=2$	Case C					
			$n=2$	$n=2.5$	$n=3$	$n=3.5$	$n=4$	$n=10$
0.900	0.44	0.83	0.52	0.47	0.44	0.41	0.40	0.32
0.950	0.65	1.16	0.74	0.66	0.61	0.56	0.54	0.39
0.980	0.94	1.61	1.04	0.92	0.84	0.77	0.72	0.48
0.990	1.17	1.96	1.27	1.12	1.01	0.92	0.86	0.55
0.995	1.40	2.30	1.50	1.31	1.18	1.07	1.00	0.62
0.997	1.57	2.56	1.67	1.46	1.31	1.19	1.08	0.66
0.999	1.94	3.11	2.03	1.77	1.58	1.43	1.32	0.76

FIG. 3.   *Curves of space factor against speed fraction for each of the three thrust assumptions.*
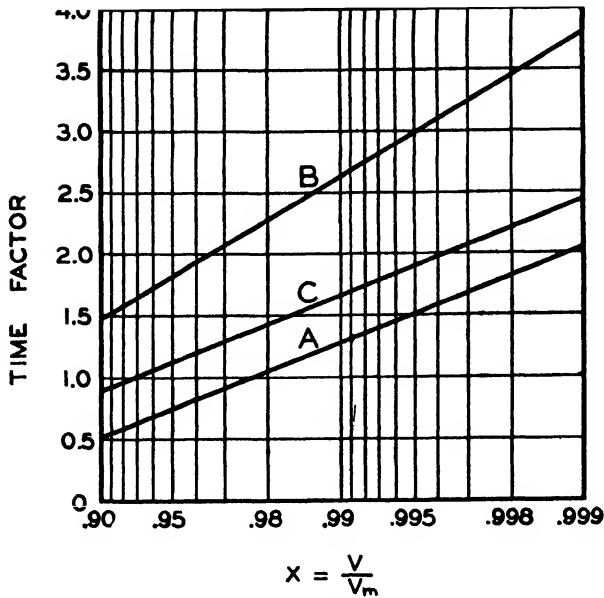
Fig. 4. *Curves of time factor against speed fraction for each of the three thrust assumptions.*

Comparison of Thrust Assumptions

A study of Figs. 3 and 4 will show that the space and time factors are of the same order of magnitude for each of the three cases. The effect of the thrust assumption is greater upon the time factor than upon the space factor. Cases A and C give nearly equal space factors, and any thrust curve (Fig. 1) lying between them will produce space factors between those shown (Fig. 3). It is believed that real thrust curves would generally fall between the A and C, but closer to the C case, so that the space factors given by the thrust assumption C are probably sufficiently accurate for general use. The variation of the time factor is determined chiefly by the thrust at very low speeds, and it is at low speeds that the three assumptions differ most. However, the time factor is not so useful as the space factor, and, moreover, if the integration of the time equations is begun at values of x far above zero, the variation diminishes greatly.

Variation of n

If the Case C thrust assumption is adopted, the effect of variation of the exponent n in the expression for resistance upon the time and space factors can be studied.

For the general case

$$F_T(x) = \int_0^x \frac{dx}{2-x-x^n}$$

and

$$F_S(x) = \int_0^x \frac{xdx}{2-x-\jmath}$$

For the specific case $x=2$, the integrals have been given, and for the case $n=3$ they are

$$F_T(x) = \tfrac{1}{8}\left[\log \frac{(2+x+x^2)}{(1-x)^2} + \frac{6}{\sqrt{7}} \arctan \frac{2x+1}{\sqrt{7}} - \log 2 - \frac{6}{\sqrt{7}} \arctan \frac{1}{\sqrt{7}}\right]$$

and $F_S(x) = \tfrac{1}{8}\left[\log \frac{(2+x+x^2)}{(1-x)^2} - \frac{10}{\sqrt{7}} \arctan \frac{2x+1}{\sqrt{7}} - \log 2 + \frac{10}{\sqrt{7}} \arctan \frac{1}{\sqrt{7}}\right]$
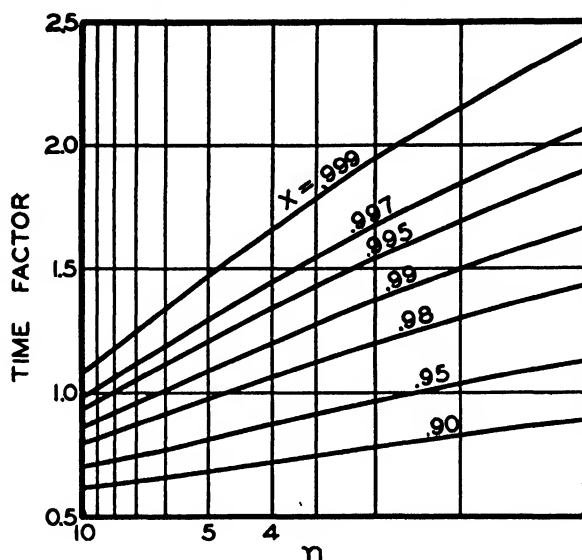

FIG. 5.   *Curves of time factor against resistance exponent for various speed fractions, using linear thrust assumption.*

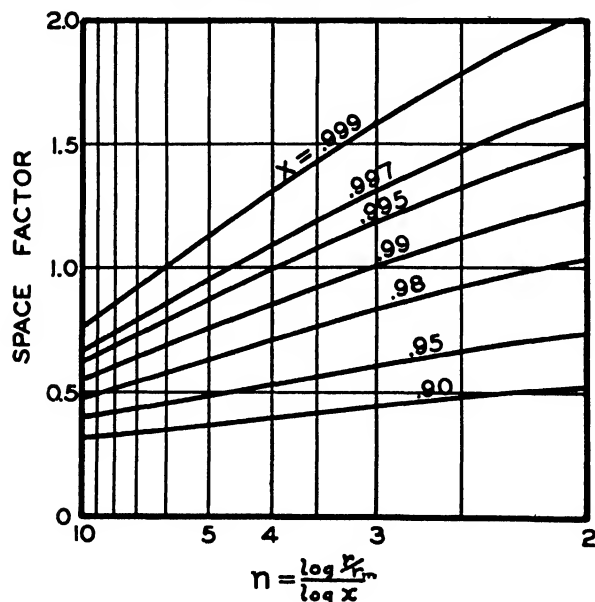$$n = \frac{\log \frac{F_r}{F_m}}{\log x}$$

FIG. 6.   *Curves of space factor against resistance exponent for various speed fractions, using linear thrust assumption. These curves are suggested for use.*

The numerical values of the space and time factors for non-integral values of n, and for integral values greater than 3, can be obtained by approximate methods for any particular value of x.   This has been done for $n = 2.5$, 3.5, 4 and 10, and the results are shown in Tables I and II.

Curves of the space and time factors plotted against n (on an arbitrary base of $1/n$ which allowed plotting the values for $n = \infty$) are shown in Figs. 5 and 6.

The interpolation for any value of n between 2 and 10 may easily be made.

Application and Numerical Example

In applying the time and space factors to a specific case the following steps must be taken.

   (i) From the design data of the ship obtain

   (a) The resistance r_m at maximum speed in pounds.

   (b) The exponent n for the variation of resistance.

   (c) The total mass to be accelerated $= 1.08 \times$ mass of ship ($m = 75 \times$ displacement of ship in long tons).

   (d) The anticipated maximum speed, v_m, in feet per second ($v_m = 1.689 \times$ max. speed in knots).

   (ii) Compute the time and space products, $\left(\dfrac{mv_m}{r_m}\right)$ and $\left(\dfrac{mv_m{}^2}{r_m}\right)$

   (iii) From Figs. 5 and 6 select the values of space and time factors for the desired speed fraction.

   (iv) Compute times and distances by multiplying products and factors found in (ii) and (iii).

Example

It is desired to know how far a certain ship must be run to attain 99.5% of its maximum speed.

The values assumed are:

$$r_m = 1{,}250{,}000 \text{ lb.}$$
$$\Delta = 80{,}000 \text{ long tons,}$$

hence

$$m = 75 \times 80{,}000 = 6{,}000{,}000 \text{ slugs,}$$
$$n = 3$$
$$v_m = 32 \text{ knots} = 32 \times 1.689 = 54 \text{ ft. per sec.}$$

The time product, $\dfrac{mv_m}{r_m} = \dfrac{6 \times 10^6 \times 54}{1.25 \times 10^6} = 259 \text{ sec.}$

The space product, $\dfrac{mv_m}{r_m} = 259 \times 54 = 14{,}000 \text{ ft.}$

From the tables, F_T (0.995) and F_S (0.995) are 1.55 and 1.18, respectively.

The time required is, therefore, $1.55 \times 259 = 402$ sec., and the space covered is $1.18 \times 14{,}000 = 16{,}500$ ft.

The above calculations are based on starting from rest.

Conclusion

It is believed that the distances computed by the above outlined methods will be useful as a guide to persons conducting speed trials of ships in ensuring that the desired speed has been obtained, without making an unnecessarily long approach run.

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NOTE ON THE EUPATHEOSCOPE AND THE MEASUREMENT OF EQUIVALENT TEMPERATURE IN CANADA[1]

By C. D. Niven[2]

Abstract

Readings have been taken on the eupatheoscope and compared with readings on thermometers and with readings on the A.S.H.V.E. effective temperature chart. It was found that the mean of the readings on two thermometers, situated one at the floor level and one at the level of the head of a sedentary worker, gave a value fairly close to the reading on the eupatheoscope. The general conclusion is reached that elaborate apparatus for reading comfort temperature is not justified until an explanation has been given of what constitutes the "freshness" of air, but that in Canada in rating comfort conditions more attention should be paid to temperature gradients, which are pronounced during spells of zero weather.

Introduction

There is perhaps no country in the world, with the exception of Siberia, to which a knowledge of indoor atmospheric conditions is of greater importance than it is to Canada. In most parts of the northern portion of the American continent windows cannot be kept wide open for at least six months of the year, and in some parts it is uncomfortable if fresh air is allowed to enter by the window during several months of the year. Such conditions put a strain on the respiratory organs which of course function most perfectly when fresh outdoor air is breathed. In spite of the obvious importance of the heating and ventilating problem in Canada, little work is being done on it. As an introduction to this work a eupatheoscope was imported from England to ascertain whether the indications it gave corresponded with the sensation of comfortable warmth felt indoors in Canada. The problem of ventilation greatly depends upon the maintenance of the conditions that give a comfortable sensation of warmth, for no matter how health-giving a ventilation scheme is, the public will undoubtedly reject it if it makes the room uncomfortably cold.

Observations taken on the eupatheoscope are given in this communication. These are compared with readings taken on thermometers.

The eupatheoscope is an instrument designed by Dufton (2). It gives a measure of the cooling power of the air in a room. It takes account of the temperature of the air, the air movement and the radiant heat energy in the room, but it does not take account of the humidity of the air. The eupatheoscope consists of a blackened cylinder about 22 in. high and $7\frac{1}{2}$ in. in diameter. The temperature of this cylinder is kept constant by means of a thermostat controlling the amount of heat supplied internally, and this amount of heat is estimated by the distance the mercury is forced down an inverted thermometer. Obviously, the more the mercury expands, the cooler the room must

be because cold atmospheric conditions imply that heat must be supplied to the cylinder in order that its temperature be kept constant. This ingenious device appeals to one because the principle on which it operates resembles the principle employed by the human body. In the human body the thermostatic control is said to be on the face, and when the face is exposed to cold the human system automatically generates more heat.

Man's feeling of comfort depends primarily on his physiological state at the moment. Therefore, any comparison between results obtained by means of a mechanical instrument and the feeling of comfort of a human being cannot be consistent.

Results

At the beginning of the investigation the readings on the eupatheoscope were compared with the effective temperatures as determined for a particular temperature and humidity from the "still air" chart in the A.S.H.V.E. guide book. It was found that the two figures differed by several degrees, and since the eupatheoscope did not take account of the relative humidity the difference was not constant. The readings are shown in the first thirteen lines of Table I. A series of readings were taken to compare the eupatheoscope readings with readings on certain thermometers placed in the following positions:—(1) outside the window close to the glass; (2) inside the window close to the glass; (3) close to the floor, near the eupatheoscope; (4) $4\frac{1}{4}$ ft. from the floor, close to the eupatheoscope. The thermometers in Positions (3) and (4) were hung from a vertical stick so that the temperature at the head and the feet of one who might be sitting at a desk would be known. It might be mentioned that the eupatheoscope and the thermometers at Positions (3) and (4) were situated about eight feet from the window and that a desk was standing between them and the window. The radiator, which was not always in use, was situated under the window.

The mean of the temperatures (Table I) read on the thermometers at the top and at the bottom of the vertical stick near the eupatheoscope differed by only a small amount from the eupatheoscope reading. On January 9, readings on the psychrometer were again begun. In the lower part of Table I a record is given of the temperatures read on the thermometers, the eupatheoscope reading, and the effective temperature as determined from the A.S.H.V.E. chart. These data substantiated the conclusions reached previously, namely, that the eupatheoscope reading did not agree with the effective temperature shown by the A.S.H.V.E. chart, but that it differed very little from the mean of the two temperatures read on the thermometers hung on the vertical stick.

The difference between the eupatheoscope reading and the reading taken from the "effective temperature" chart is given in Table I. It is interesting to note that the large differences between these two figures arise generally when the room temperature is high. Thus it can be understood that in England the eupatheoscope is a better indicator than it is in Canada because the houses

TABLE I

Date	Wind	Temp. outside window, °F.	Temp. inside window, °F.	Temp. on floor, °F.	Temp. at head, °F.	Mean temp. at floor and head, °F.	Room temp. on desk, °F.	Room humidity	Effective temp., F°.	Eupatheoscope reading	Eupatheoscope—Eff. temp., °F.	Mean temp., °F., at floor and head—eupatheoscope	Head-floor temps., °F.	Remarks
Sept. 12							73.5	61	70	75	5			
15							74	65	70.5	76.5	6			
17							72.5	53	68	73.5	5.5			
18							69	47	65	68.5	3.5			
19							70	55	66.5	69	3.5			
20							69	59	65.5	67.5	2.0			
Oct. 2							67	45	63.5	65	1.5			
3							67	53	63.5	66	2.5			
4							67	49	63.5	64	0.5			
5							67	45	63.5	65	1.5			
7							65	44	61.5	65	3.5			
16							67	41	63	66	3.0			
Nov. 14							62	34	59	61	2.0			
Dec. 5		27	55	61	62	61.5				61.5		0	1.0	
6	NW	18	52	60	62	61				60.5		0.5	2.0	
6		17	55	61	63	62				62		0	2.0	
7	NW	8	50	57	60	58.5				59		0.5	3.0	
8	NE	6	52	57	60	58.5				58.5		0	3.0	
10	NW	13	72	63.5	68	66				65.5		0.5	4.5	Rad. on
10		20	55	61	63.5	62.5				62.5		0	2.5	Rad. off
11	N	8	53	58	62	60				59.5		0.5	4.0	Rad. off
11		20	80	64.5	67.5	66				65.5		0.5	3.0	Rad. on
11		18	56	62	64	63				63.5		0.5	2.0	Rad. off
12	N	16	55	60	62	61				61		0	2.0	
13		28	56	60.5	63	62				62		0	2.5	
14	N	22	54	59	61.5	60.5				60.5		0	2.5	
15	WNW	8	42	56	60	58				58.5		0.5	4.0	
17		21	80	71	73	72				72.5		0.5	2.0	Rad. on
18	W	6	48	61	64	62.5				63		0.5	3.0	
19	E	22	88	72	75.5	74				74		0	3.5	Rad. on
20		20	65	70	71	70.5				69.5		1.0	1.0	Rad. on
21	E	16	64	71	73	72				72.5		0.5	2.0	Rad. on
22	N	12	82	71.5	74	73				73		0	2.5	Rad. on
25	No wind	19	86	73	75	74				74		0	2.0	Rad. on
26		− 6	49	55	59	57				57		0	4.0	
27	E	12	88	70	74	72				73		1.0	4.0	Rad. on
28	E	17	58	63	66	64 5				63.5		1.0	3.0	
31		− 3	46	53	57	55				55		0	4.0	
Jan. 2	NW	− 5	60	63	70	67.5				67		0.5	7.0	Rad. on
3	NE	12	60	70	72.5	71.5				71.5		0.0	2.5	Rad. on
4	NW	−12	57	69	75	72				73		1.0	6 0	Rad. on
5	NE	1	66	73	78	75.5				77		1.5	5.0	Rad. on
7		43	68	74	76	75				75.5		0.5	2.0	Rad. on
7		46	66	62	66	64				66		2.0	4.0	Window open.
8		43	85	72	74	73				73.5		0.5	2.0	Rad. on
9	N	33	62	67	68.5	68	69	32	64.5	67.5	3.0	0.5	1.5	
10		40	65	68.5	69.5	69	70	33	65	68.5	3.5	0.5	1.0	
11	NW	21	54	62	65.5	64	66	21	61	64.5	3.5	0.5	3.5	
12	N	2	51	59	62	60.5				60		0.5	3	
12		3	59	62	65.5	64	64	15	60	64	4.0	0	3.5	Rad. on
14	N	12	73	71.5	75	73.5	73.5	13	66	73.5	7.5	0	3.5	Rad. on
15	NE	− 1	78	72	77	74.5	76	16	68.5	76	7.5	1.5	5	Rad. on
16	N	3	57	64	68	66	67	21	62	66	4	0	4	
17	SE	10	57	63	66	64.5	64.5	23	60.5	64.5	4	0	3	
19		0	58	66	68.5	67	68	20	63	67	4	0	2.5	
21	E	28	64	69	70	69.5	70	25	64.5	69	4.5	0.5	1.0	
22	N	4	53	64	66	65	65	27	60	64	4	1.0	2.0	
23	NE	2	56	63	68	65.5	67	20	62	66	4	0.5	5.0	Door open
24	NE	−14	45	69	73	71	71	17	64.5	70.5	6	0.5	4.0	Rad. on
25	W	− 5	92	71	76	73.5	75	12	67	74	7	0.5	5.0	Rad. on
26	N	− 1	60	72	76	74	74	20	67	74	7	0	4 0	

in England are usually kept at temperatures ranging from 60° to 66° F., not at 72° F. Another point of interest is the fact that the temperature gradient given in the second last column of the table is greatest during the periods when the outdoor temperature is lowest. Some observations made during the summer, which are not reported here, serve to accentuate this. During the summer the temperature gradient was usually zero or one degree.

During the following winter more observations were taken, and these are given in Table II. As the wind directions and the readings on the thermometer placed inside the window were not useful, they were not noted. The correspondence between the eupatheoscope reading and the mean of the two thermometers on the stick is not so good in this table. It would appear, however, that this is not entirely a contradiction of our inference from Table I, since the table shows that it is just when the agreement between those figures was poor that the eupatheoscope reading differed less than usual from the effective temperature reading. Since the eupatheoscope did not appear to hold its calibration accurately, one is inclined to think that the readings on it were at times too high. In this connection it is interesting to note that if 4 be subtracted from the mean of the readings on the thermometers, the resulting figure does not differ very much from the effective temperature readings recorded in Table II.

One is inclined, therefore, to believe that two thermometers, one hung vertically above the other with their bulbs $\frac{1}{4}$ in. and $4\frac{1}{4}$ ft. from the floor, give an indication of the equivalent temperature in a room in which there is comparatively little air movement, no strong sources of heat radiation and not too extreme temperatures and humidities. Thus the thermometers supply in a simple manner the information that the eupatheoscope or the A.S.H.V.E. chart would supply under the said restricted conditions. The fact that the eupatheoscope did not hold its calibration well, detracts from its suitability, while the use of the A.S.H.V.E. chart necessitates the use of a psychrometer. Thermometers placed vertically one above the other in this way give an estimate of the temperature gradient, which is information of substantial importance in the evaluation of comfort conditions for the sedentary worker.

Sir Leonard Hill pointed out that a higher cooling power on the feet than on the head gives rise to discomfort, yet no account of this is usually taken in discussing comfort temperatures. In addition to room temperature, relative humidity and air movement, it is desirable in determining conditions for comfort in the winter time to take into account the temperature gradient, or, to be more accurate, the "cooling power gradient". The discovery of the large temperature gradients in the room to which the above data refer explains why the room felt uncomfortably cold even when the thermometer reading was high enough.

In an article (1, p. 55) by Angus the uncomfortable effect of high cooling power on the feet is stressed. Referring to an investigation on board ship he writes:—"But the dynamo-room was considered to be the most uncomfortable

TABLE II

Date		Temp. outside window, °F.	Temp. on floor, °F.	Temp. at head, °F.	Mean temp. at floor and head, °F.	Room temp. on desk, °F.	Room humidity	Effective temp., °F.	Eupatheoscope reading	Eupatheoscope —Eff. temp., °F.	Mean temp. (°F), floor and head—eupatheoscope	Head-floor temps., °F.
Aug.	31	61.0	70.0	71.0	70.5	71.0	48.0	66.5	68.0	1.5	2.5	1.0
Sept.	5	67	70	71	70.5	71	52	67	67.5	0.5	3.0	1.0
	6	60	70	70	70	70	55	66.5	67.5	1.0	2.5	0
	7	59.5	70	70	70	70	51	66	67	1.0	3.0	0
	19	68	73	73	73	73	65	70	73	3.0	0	0
	20	60	72	73	72.5	73	63	69.5	73.5	4.0	1.0	1.0
	21	58	72	73	72.5	72.5	53	68.5	72.5	4.0	0	1.0
	23	46	67	69	68	69	47	65	67.5	2.5	0.5	2.0
	24	52	68	70	69	70	51	66	68.5	2.5	0.5	2.0
	25	57	69	70	69.5	70	51	66	69	3.0	0.5	1.0
Oct.	31	51	72	72	72	72	49	67.5	70.5	3.0	1.5	0
Nov.	1	51	71	72	71.5	71	45	66.5	70.5	4.0	1.0	1.0
	2	43	70	71	70.5	70	51	66	69.5	3.5	1.0	1.0
	4	48	68	68.5	68	68	38	64	67	3.0	1.0	0.5
	5	62	70	70	70	70	55	66.5	69	2.5	1.0	0
	6	41	68	69	68.5	69	39	64.5	68	3.5	0.5	1.0
	7	39	70	71	70.5	71	33	65.5	70	4.5	0.5	1.0
	8	45	70	72	71	71	33	65.5	71	5.5	0	2.0
	9	37	70	72	71	71	30	65.5	70	4.3	1.0	2.0
	12	36	72	73	72.5	72.5	34	67	72	5.0	0.5	1.0
	13	38	68	70	69	69	35	64.5	68	3.5	1.0	2.0
	14	41	68	69	68.5	69	35	64.5	67	2.5	1.5	1.0
	15	39	66	67	66.5	67	37	62.5	65	2.5	1.5	1.0
	16	32	64	65.5	65	65	35	61.5	63	1.5	2.0	1.5
	18	32	64	65	64.5	65	27	61	62.5	1.5	2.0	1.0
	19	34	66	67	66.5	66	29	61.5	64	2.5	2.5	1.0
	20	45	68.5	69.5	69	68.5	47	65	67.5	2.5	1.5	1.0
Dec.	17	19	61	63	62	62	20	58	60.5	2.5	1.5	2.0
	18	26	63	66	64.5	65	44	61.5	62.5	1.0	2.0	3.0
	19	28	67	69	68	67	33	62.5	66	3.5	2.0	2.0
	20	18	66	68	67	67	30	62.5	66	3.5	1.0	2.0
	21	0	58	63	60.5	60 5	15	57	60	3.0	0.0	5.0
	23	0	59	63	61	60.5	20	57	60	3.0	1.0	4.0
	26	6	59	62	60.5	60	21	57	58.5	1.5	2.0	3.0
	27	12	57	60	58.5	58	23	55.5	57	1.5	1.5	3.0
	28	−3	55	59	57	57	17	55	55.5	0.5	1.5	4.0
	30	0	58	62	60	60	17	57	57.5	0.5	2.5	4.0
	31	8	62	65	63.5	63	21	59	61	2.0	2.5	3.0
Jan.	2	32	64	66	65	65	24	61	63	2.0	2.0	2.0
	3	36	66	68	66	67	26	62	64.5	2.5	1.5	2.0
	4	36	66	67	66 5	66.5	27	62	64.5	2.5	2.0	1.0
	7	32	68	70	69	68	23	63	67	4	2.0	2.0
	8	13	64	67	65.5	65	24	60.5	64	3.5	1.5	3.0
	9	22	65	67	66	64	26	60	64	4	2.0	2.0
	10	34	66	68	67	67	26	62	64.5	2.5	2.5	2.0
	11	34	65	68	66.5	66.5	26	62	64.5	2.5	2.0	3.0
	13	32	67	69	68	68	31	63.5	67	3.5	1.0	2.0
	14	2	59	63	61	61	27	57.5	60	2.5	1.0	4.0
	15	16	62	65	63.5	63	25	59.5	61.5	2.0	2.0	3.0
	16	8	58	62	60	60	21	57	57.5	0.5	2.5	4.0
	17	4	61	63	62	63	17	59	60	1.0	2.0	2.0
	18	8	71	75	73	74	17	66.5	71	4.5	2.0	4.0
	20	6	58	62	60	60	21	57	57	0	3.0	4.0
	21	4	72	76	74	75	18	67	72.5	5.5	1.5	4.0
	22	30	64	67	65.5	66	29	60.5	63.5	3.0	2.0	3.0
	23	−6	54	59	56.5	57	14	54.5	57	2.5	0.5	5.0
	24	−8	65	70	67.5	69	43	65	64.5	0.5	3.0	5.0

part of the engineers" 'tween decks'. Here I found that although on the days in question the temperature was only two degrees above that in the engine-room with the fans on, a very high air velocity along the deck was causing a reversal of cooling powers—hot heads and cold feet."

The fact that the human thermostat is situated on the face makes a high temperature gradient disagreeable for anyone whose feet cool easily. The writer asked a number of persons whether they complained first of cold on the feet or cold on the body, and there was found to be a considerable difference of opinion, while many could not answer at all. Nevertheless the evidence of both Hill and Angus is sufficient to warrant the consideration that temperature gradient is an item that must be taken into account by a physical instrument designed especially to measure comfort conditions, particularly in localities exposed to subzero weather.

Conclusions

To sum up, it may be said that the work indicated that the eupatheoscope did not give results agreeing with A.S.H.V.E. chart: the disagreement was largest when the temperature was high and the humidity low: on such days the temperature gradient was often large. In England, where the eupatheoscope was developed, these gradients would not be nearly so important as in Canada, since it is during subzero weather that they are as a rule largest. The instrument that would be required in Canada would need to be one in which temperature gradient was taken into account, as well as the mere cooling power of the air.

Such an instrument would undoubtedly be rather elaborate; strictly speaking it should measure the cooling power of the air at the feet as well as at the head. But even if it were constructed it might still not give an estimate of comfortable indoor atmospheric conditions as it would not detect the effect of air-conditioning processes which render the air often disagreeable for the respiratory organs or what is colloquially known as "dead". For this reason one is inclined to wonder whether the designing of elaborate apparatus for determining comfort temperatures is advisable until an answer is given to the much more important question of what causes air to feel "dead". If conditions in a room are such that the air movement is small, the temperature around 66° F. so that humidity is not of great importance, and with no strong sources of heat radiation present, the work described points to the possibility that two thermometers placed at head level and at foot level will give a fair indication of whether the room is comfortable.

Since the beginning of this work the eupatheoscope Mark II (3) has been developed, but as the general principle upon which it operates is similar to that of the eupatheoscope discussed in this note, it is not considered probable that, by having substituted it for the eupatheoscope used by the writer, very different conclusions would have been reached.

The "Rutledge Pure Air" System

After the completion of the observations on the eupatheoscope, a system developed by R. Rutledge, called the "Rutledge Pure Air", was examined to observe its effect on the freshness of the air in a room. Some measurements were made on the temperature gradient and the relative humidity in the room containing the installation, as well as in two other rooms for comparison. Owing to the fact already mentioned, that the temperature gradient has a bearing on "comfort" temperature, a description of this work and the results are given.

The Rutledge system consists in placing shallow pans very close to the ceiling and circulating water through them. In this way a very large surface of fresh water is exposed to the air of the room at the very part where warm vitiated air collects. The system was not devised primarily for occupied rooms but for cold stores, and it is claimed that in a cold store where it is installed products such as meat keep in much better condition than in ordinary cold stores. If this statement be correct, it is reasonable to suppose that the system should keep the air of a room fresher. The installation of the pans over about half the area of the ceiling of the room in which the work on the eupatheoscope was carried out has had very noticeable effects. Non-technical visitors to the room have remarked that they noticed the difference at once when they entered. One visitor remarked that it felt quite "exhilarating".

To give a scientific explanation of this is not easy; several possibilities suggest themselves. The first is that the humidity was higher; but then in reply to this suggestion one may argue that the very best humidifying systems in air-conditioned houses do not necessarily give the exhilarating feeling but sometimes the reverse. A second suggestion is that the cold water circulating overhead reduced the temperature gradient. Evidence to this effect has been found, and is presented in Tables III, IV and V. But it is not entirely conclusive. A third suggestion is that by humidifying the air in the room a lower temperature was found comfortable. A fourth suggestion is that radiation was taking place from the subject to these cold pans, and as the head was nearer to the pans than were the feet the effect was somewhat similar to an inversion of the ordinary temperature gradient. Thermometers hung in the air would not have registered this effect. A fifth suggestion is that the effect was due to some phenomenon not as yet understood, but connected with the passing of air over moving water. Mr. Rutledge himself favors this idea.

The fact remains, however, that whatever the cause may be, the effect was present. The room A, in which the pans were installed, was compared with two other rooms. One of these, B, was next to it in the building and was therefore exposed to similar winds, while the other, C, was on the other side of the building. The radiator in C was kept on all the time, but in A and B it had to be turned off at times and the windows opened. In room A, the temperature at 9 a.m. was usually intolerably warm, and the plan was adopted of

TABLE III
Room *A*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 28	8	71	72.3	74.7	1.3	3.7	61	Radiator on overnight
Jan. 29	26	70.4	71.3	72.5	0.9	2.1	66	Radiator on overnight
Feb. 2	7	65	67.1	68	2.1	3.0	45	Radiator on overnight
Feb. 3	6	67	69.3	71	2.3	4.0	44	Radiator on overnight
Feb. 4	10	71.5	73.5	75.5	2.0	4.0	54	Radiator on overnight
Feb. 5	20	73	74.3	76.3	1.3	3.3	62	Radiator on overnight
Jan. 27	0	63	64.3	64	1.3	1.0	54	Radiator off overnight
Jan. 30	18	62.3	62.6	63.4	0.3	1.1	55	Radiator off overnight
Feb. 1	30	60	60.1	60.2	0.1	0.2	58	Radiator off overnight
Jan. 27		65.5	67.8	70	2.3	4.5		1 hr after radiator turned on
Jan. 27		66.5	69.3	71	2.8	4.5		2 hr. after radiator turned on
Jan. 27		65.2	66.3	67	1.1	1.8		1 hr. after radiator turned off
Jan. 28		71	71.3	71.9	0.3	0.9		½ hr. after radiator turned off
Jan. 28		66.7	68.5	70	1.8	3.3		Radiator off and window opened 2 in.
Jan. 28		61	66.3	67	5.3	6.0		Window opened wide; then closed
Jan. 28		65.5	66.2	67.9	0.7	2.4		40 min. later
Feb. 2		59.2	61.3	62.4	2.1	3.2		Radiator off; afternoon readings
Feb. 3		63.5	64.3	65.1	0.8	1 6		Radiator off; afternoon readings
Feb. 4		67.5	67.5	68.1	0	0.6		Radiator off; afternoon readings

TABLE IV
Room *B*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 27	0	65.7	69.5	74.4	3.8	8.7	19	Radiator on overnight
Jan. 28	8	67.5	71	74.2	3.5	6.7	16	Radiator on overnight
Jan. 29	26	68.7	72	74.2	3.3	5.5	20	Radiator on overnight
Feb. 2	7	60.7	65.2	68.2	4.5	7.5	15	Radiator on overnight
Feb. 3	6	64.9	68	70.2	3.1	5.3	15	Radiator on overnight
Feb. 4	10	70.2	74.5	77.5	4.3	7.3	18	Radiator on overnight
Feb. 5	20	72.5	75.5	79.4	3.0	6.9	24	Radiator on overnight
Jan. 30	18	62.7	64.5	67.2	1.8	4.5	25	Radiator off overnight
Feb. 1	30	60.7	62.5	64.7	1.8	4.0	24	Radiator off overnight

TABLE V
Room *C*

Date	Outdoor temp., °F.	Temp. on floor, °F.	Temp. at head, °F.	Temp. at ceiling, °F.	Head-floor, °F.	Ceiling-floor, °F.	Rel. hum., %	Remarks
Jan. 27	0	72.5	75.7	81.4	3.2	8.9	22	Radiator on overnight
Jan. 28	8	71.6	75.1	78.9	3.5	7.3	15	Radiator on overnight
Jan. 29	26	67.8	71.8	75.9	4.0	8.1	15	Radiator on overnight
Jan. 30	18	68.7	74	79.6	5.3	10.9	14	Radiator on overnight
Feb. 1	30	68.7	70	72.9	1.3	4.2	20	Radiator on overnight
Feb. 2	7	70.2	72	76.3	1.8	6.1	15	Radiator on overnight
Feb. 3	6	71.4	76	80.9	4.6	9.5	10	Radiator on overnight
Feb. 4	10	74.5	76.8	81.4	2.3	6.9	10	Radiator on overnight
Feb. 5	20	70.8	73.2	77.4	2.4	6.6	13	Radiator on overnight

cooling off the room, turning off the radiator and allowing the temperatures to adjust themselves. Readings were taken in the afternoon. On the three occasions on which the radiator was off overnight in room A, low gradients were found in the morning. So many factors enter into a full discussion of these data that it is unwise to draw too definite conclusions from them, but the general impression is given that the temperature gradient was smaller in room A than in either of the others. The temperature difference between the head and the feet of a sedentary worker was about twice in the one case what it was in the other; furthermore, the relative humidity in room A was about three or four times as high as in B or C. From Table III it is clear that keeping the radiator on, increased the temperature gradient. Since opening a window introduces a cold layer of air on the floor of a room, the conventional practice of keeping the window open and the radiator on creates a large temperature gradient, and therefore, according to both Hill and Angus, keeps the room uncomfortable. It is clear that further investigation along these lines should be carried out.

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AN ATTEMPT TO DETECT THE PRESENCE OF METASTABLE ATOMS IN ACTIVE NITROGEN BY LIGHT ABSORPTION[1]

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Abstract

In order to explain the nitrogen afterglow, Cario and Kaplan have assumed the presence of metastable ^{2}D and ^{2}P atoms in active nitrogen. The nitrogen emission lines at 1492Å and 1742Å have these metastable states as lower states, and should therefore be absorbed by active nitrogen. However, no absorption has been found by the writers. This leads to 1/6000% as an upper limit for the stationary concentration of metastable atoms in active nitrogen, which is compatible with the experiments. In order to account for the observed intensity of the afterglow, on the basis of Cario-Kaplan's theory, a lifetime of the metastable ^{2}P atoms $\leq 8 \times 10^{-4}$ sec. has to be assumed and a concentration of metastable molecules greater than 1/330%.

Introduction

According to the theory put forward by Cario and Kaplan (1), active afterglowing nitrogen contains, besides normal nitrogen atoms in the ^{4}S state, also nitrogen atoms in the metastable ^{2}D and ^{2}P states, 2.37 and 3.54 volts respectively above the ^{4}S groundstate, and metastable nitrogen molecules in the $A^3\Sigma$ state. The excitation of the visible afterglow bands in particular (upper state $B^3\Pi_g$) according to Cario and Kaplan is due to the collision of a nitrogen $A^3\Sigma$ molecule with a ^{2}P nitrogen atom. In fact the energy of the highest vibrational state excited in the production of the afterglow bands agrees very nearly with the energy of a nitrogen molecule ($A^3\Sigma$) + a nitrogen atom (^{2}P). If this explanation is correct, one would expect a certain stationary concentration of ^{2}P nitrogen atoms in nitrogen that shows the afterglow. Indeed, Jackson and Broadway (4), a number of years ago, found the presence of ^{2}P nitrogen atoms in a Stern-Gerlach experiment with a molecular beam taken from active nitrogen. It seemed puzzling, however, that they observed only the $^2P_{3/2}$ component of the ^{2}P term and not the $^2P_{1/2}$ component, and that there was no indication of the ^{4}S state. The writers therefore thought it worthwhile to try to find evidence for the presence of the metastable atoms by an entirely different method, namely, by the absorption of light from the metastable states.

Experimental

The lines of longest wave-length that can be absorbed by the ^2P and ^2D states are the doublet at 1742Å and the doublet at 1492Å, respectively. Thus a vacuum spectrograph had to be used. If a continuous spectrum is used as a background for the absorption experiments, rather high resolution has to be used in order to observe narrow and faint absorption lines (3). Instead the writers used the emission lines of nitrogen as a background because the only spectrograph available to them was a small Cario-Schmidt-Ott. Evidently the sensitivity of the test does then not depend on the dispersion of the spectrograph. The emission lines of N I were produced in a powerful uncondensed discharge through nitrogen. After the tube was operated for a while the nitrogen lines came out very strongly in emission, and could be photographed within a few minutes when the distance between the discharge tube and the slit of the spectrograph was 60 cm.

The afterglowing nitrogen was pumped from a condensed discharge, at a pressure of about 6 mm., through the absorption tube of 60 cm. length and 8 mm. diameter placed between the spectrograph and the background discharge tube. Thin crystalline quartz windows, transparent to 1450Å, were used to separate the absorption tube from the spectrograph and the light source. The exciting discharge of the active nitrogen was as near as possible to the absorption tube and the intensity of the afterglow for at least 10 to 20 cm. of the absorption tube was so great that its spectrum appeared on the plates for exposure times of only 10 min. (aperture of spectrograph, 1 : 10).

Results and Discussion

No difference in the intensities of the nitrogen doublets at 1742Å and 1492Å could be detected between exposures taken when the nitrogen passing through the absorption tube was activated and when it was not. That is, *no absorption of these lines was found.* This does not necessarily mean that there are no metastable atoms in active nitrogen, but it does prove that if they are present their concentration must be low. It is possible to deduce an upper limit to this concentration for the experimental arrangement used.

It seems safe to assume that the f-value (number of dispersion electrons) for the lines 1742Å ($2p^2P–3s^2P$) and 1492Å ($2p^2D–3s^2P$) is of the order 0.1, the transition being entirely allowed and involving low values of the principal quantum number only. Therefore, it follows that the absorption coefficient for the centre of the line at atmospheric pressure (6) is of the order, $k_o^{760} = 10^7$. Since the intensity of the afterglow decreased appreciably along the absorption tube of 60 cm. length, an absorbing length of only 10 cm. was assumed. It can be stated with certainty that a 50% decrease of intensity of the nitrogen emission lines would have been observed. It follows that the absorption coefficient k_o^p for the actual partial pressure of nitrogen ^2P and ^2D atoms, respectively, must have been smaller than 0.16. In deriving this value, consideration was given to the fact that the emission and the absorption

lines have different Doppler widths, owing to the difference in the temperatures involved (5, p. 1021). The ratio $\dfrac{k_o{}^p}{k_o{}^{760}}$ gives the maximum partial pressure of ^2D and ^2P atoms that is compatible with the observed fact that no absorption by these states was noticeable. This upper limit is 1×10^{-5} mm. or 4×10^{11} $^2P(^2D)$ atoms per cc.

Experiments by Wrede (7, p. 65) and others have shown that active nitrogen produced in the ordinary way contains about 1% atoms. This corresponds to a partial pressure of 0.06 mm. in the present experiments. Thus it is seen that the ^2P and ^2D atoms, if present at all, form only a minute fraction, less than 1/6000, of the atomic part of active nitrogen.

By comparison with a calibrated mercury arc the number of quanta emitted in the green, yellow and red by active nitrogen was determined roughly. The writers found 5×10^{14} quanta per cc. per sec. Since according to Kaplan and Cario's theory every quantum of the *visible* afterglow bands is emitted by the action of one ^2P atom, it follows that the stationary concentration on the basis of this theory in the experiment must have been larger than 5×10^{14} τ per cc., where τ is the average lifetime of a ^2P atom. But (see above) the negative result of the absorption experiments shows that the number of ^2P atoms is smaller than 4×10^{11} atoms per cc., hence it follows that

$$\tau \leqq 8 \times 10^{-4} \text{ sec.}$$

A lower limit for the number of $A^3\Sigma$ molecules may be derived (assuming that there is no abnormal collision radius) if the limitation of the lifetime is due entirely to collisions with $A^3\Sigma$ molecules and subsequent production of the visible afterglow. A value 6.5×10^{12} atoms per cc. (1.8×10^{-4} mm.) is obtained. This value is about 16 times larger than the maximum number of ^2P atoms which is compatible with the writers' experiments but about 330 times smaller than the number of normal atoms. It should be noted that the number of $^3\Sigma$ molecules is derived on the assumption that Cario and Kaplan's theory is correct, whereas the upper limit for the number of ^2P atoms derived is independent of this assumption.

Thus, of active nitrogen 1% is normal atoms, less than 1/6000% is mestastable atoms and, if the Cario-Kaplan theory is right, 1/330% or more is metastable $A^3\Sigma$ molecules. As is seen, the unexpectedly low concentration of metastable atoms as found in these experiments does not necessarily contradict the Cario-Kaplan theory if there is a suitable concentration of metastable $^3\Sigma$ molecules. Yet the concentration of the metastable molecules can be so low that it will be practically impossible to prove their presence by absorption experiments.* It should be easy, however, to detect the presence of *normal* atoms by absorption if it were not for the fact that the resonance lines lie at 1190Å, which makes the experiment impossible for the fluorite spectrograph used.

Frost and Oldenberg (2) were unable to find absorption by metastable molecules in a discharge which they thought has a greater concentration of metastable molecules than active nitrogen.

The results obtained are evidently in disagreement with the Stern-Gerlach experiment by Jackson and Broadway (4) because, according to the above, normal ^4S atoms constitute by far the largest part of active nitrogen and they would give quite a different Stern-Gerlach pattern from that observed by Jackson and Broadway. The possibility that their method of detection was sensitive only to ^2P atoms and not to ^4S atoms seems rather remote, and the difficulty that they observed only $^2P_{1/2}$ atoms and no $^2P_{3/2}$ atoms would even then remain.

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ABSORPTION CURVES AND RANGES FOR HOMOGENEOUS β-RAYS[1]

By J. S. Marshall[2] and A. G. Ward[3]

Abstract

β-rays were bent in a uniform magnetic field, after which they entered, as approximately homogeneous rays, an ionization chamber connected to a linear amplifier. Absorption curves in aluminium were determined for various values of $H\rho$. The active materials were radium E and uranium X.

Apparatus

The β-ray spectrometer consisted of an evacuated brass box, 22 by 14 by 4 cm., placed between the poles of an electromagnet that practically gave a uniform field over the path of the β-rays in the box. Two slits were used, one to define the angular width of the beam, the other to reduce scattered radiation from the walls of the box, this scattered radiation being further reduced by lining the walls with cardboard. Both slits limited the beam to a width of 1 cm. in planes parallel to the direction of the magnetic field. The window of the spectrometer was 10 by 5 mm. It was covered with one layer of ordinary cellophane of 0.00318 gm. per sq. cm. β-rays that emerged from the spectrometer possessed radii of curvature varying from 6.80 to 7.20 cm., the average radius being 7.00 cm. In most of the experiments, the window of the ionization chamber was 7 cm. distant from the window of the spectrometer. The strengths of the magnetic field could be measured with an error less than $\frac{1}{4}$ of 1%. The value of ρ taken is correct to $\frac{1}{3}$ of 1%.

The ionization chamber was made of steel, 14 cm. inner diameter and 13 cm. deep. It was filled with carbon dioxide at atmospheric pressure. The window was covered with two layers of cellophane, the outer layer waterproof, the inner layer ordinary cellophane coated with drawing ink to make it conducting. The mass per square centimetre of the window was 0.00690 gm. Ionization currents could be measured accurately to 2×10^{-16} amp. by means of an F.P. 54 pliotron in an amplifying circuit devised by DuBridge and Brown (2).

Results

Some typical absorption curves are shown in Fig. 1, allowance being made for the materials the β-rays had to pass through from the spectrometer to the ionization chamber. Each curve is initially concave towards the axis of abscissas, the linear part is fairly well defined and there is quite an appreciable tail on the curve. The linear part of each curve has been extended so as to cut the axis of abscissas, and the point where it cuts the axis has been called the extrapolated range in gm. per sq. cm. of aluminium for β-rays of
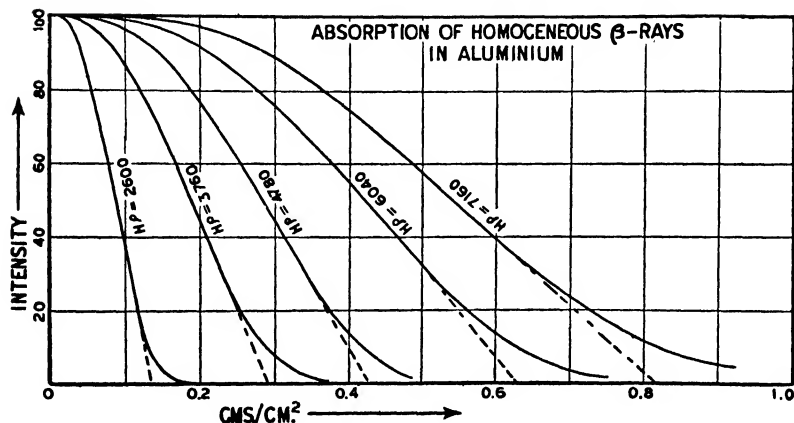
FIG. 1.

the given $H\rho$. It is customary to do this, but it cannot really be justified, the real range being considerably greater as can be seen when one considers the narrow range in $H\rho$ for each beam, *viz.*: from 6.8 to 7.2 H and the appreciable tail on each absorption curve.

The ranges determined in the manner described above have been plotted against $H\rho$ (Figs. 2 and 3). Schonland (5), Varder (6), Madgwick (4) and Eddy (3) have determined similar ranges for β-rays in aluminium and, for
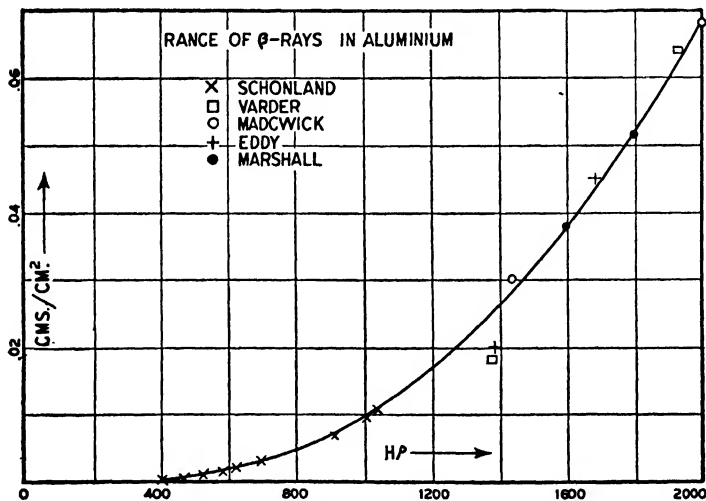
FIG. 2.

the sake of completeness, their results are also given. It will be noticed that our results lie midway between those of other experimenters. The initial portions of the curves obtained by us correspond to those on similar curves obtained by Crowther (1) and Wilson (7), but differ markedly from those obtained by Varder and Madgwick. This is due, no doubt, to differences in

EXTRAPOLATED RANGES FOR HOMOGENEOUS
β-RAYS IN ALUMINIUM
□ VARDER
○ MADGWICK
+ EDDY
● MARSHALL
▲ WARD
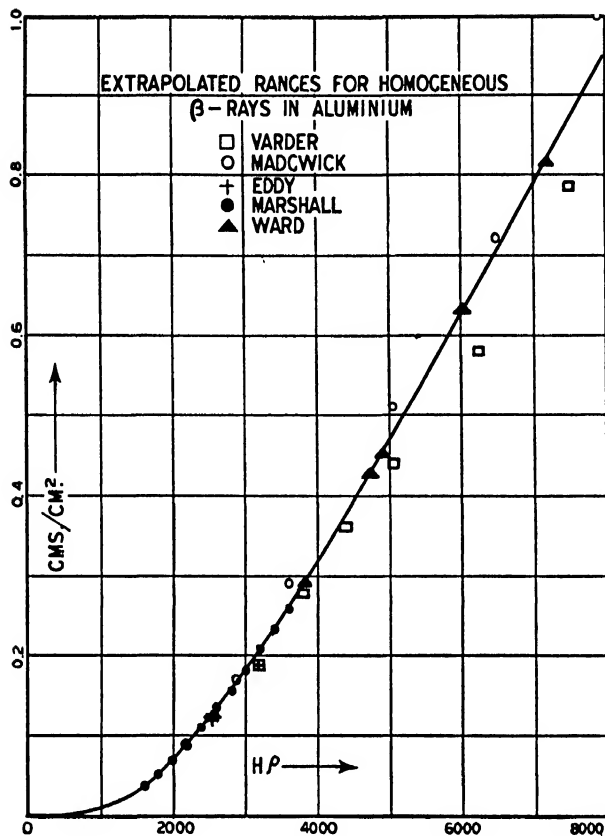
FIG. 3.

the experimental conditions, but it is felt that curves such as those given in Fig. 1 correspond more closely to what actually happens and they are certainly more useful to other experimenters.

Acknowledgment

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THE END POINTS OF THE β-RAY SPECTRA OF RADIUM E AND URANIUM X_2[1]

By A. G. Ward[2] and J. A. Gray[3]

Abstract

The end points of the β-ray spectra of radium E and uranium X_2 have been measured, using semi-circular magnetic focusing and an ionization chamber connected to a linear amplifier. Experimental results give end points of $H\rho = 5250$ gauss-cm. for radium E and $H\rho = 9300$ gauss-cm. for uranium X_2.

Introduction

It was shown indirectly by Gray (2) in 1913 that the β-rays of radium E should have a definite end point. He found that when these β-rays were absorbed by paper, after a while, they became more and more absorbable, showing that they had a definite range. A magnetic field was used to distinguish between β- and γ-rays. As he pointed out then, a similar result could be deduced from earlier experiments by Schmidt (7). The fact that there is a definite range is shown even more clearly by the later experiments of Gray and Henderson (3).

Experimental

For some time the writers have been observing the properties of β-rays scattered through large angles by thin metallic foils, and to aid in the interpretation of these experiments it has been found necessary to determine the distribution of β-rays in the spectra of the active materials used, radium E and uranium X_2. While the writers were obtaining these spectra, it was thought worth while to measure the end point, or maximum value of the energy or momentum ($H\rho$) of these β-rays, as accurately as possible. The apparatus that was used was exactly the same as that described by Marshall and Ward (6). The results for radium E (radium D was used as a source) are shown in Fig. 1, in which the ionization obtained with a definite value of magnet current is plotted against that current. It will be noted that in each graph there are two curves, the lower curve indicating the intensity when an aluminium absorption sheet, 0.175 gm. per sq. cm., was placed in front of the ionization chamber. This was done so that one could distinguish clearly between scattered radiation and radiation that was due to the bending of the rays in the magnetic field. Near the end point, this absorption sheet reduces the intensity of the radiation to 80% of its initial value.
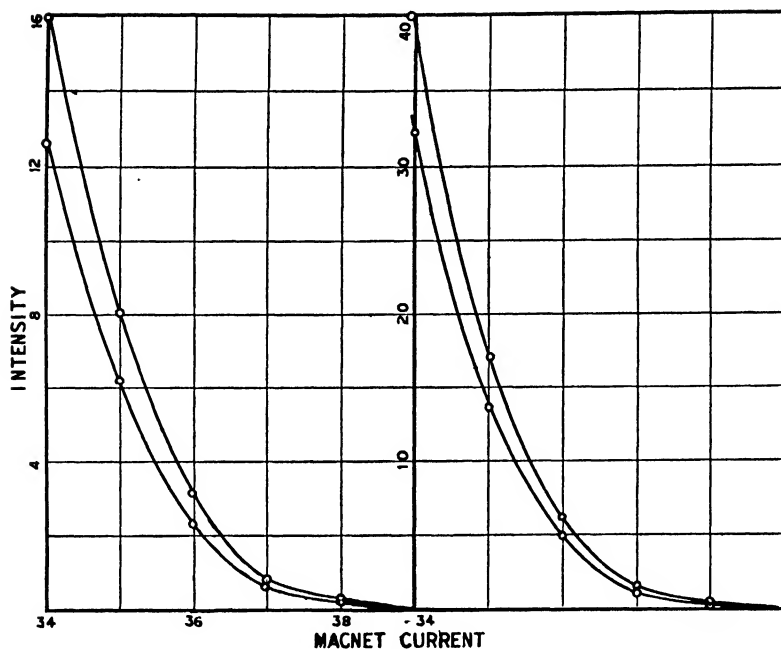
FIG. 1.

Results

The first graph shows the results obtained when the slit limiting the angular width of the beam in the spectrometer was $\frac{1}{2}$ in. wide, the second when the same slit was 1 in. wide and the spectrometer somewhat nearer the ionization chamber. As a result the intensities in the latter case are about two and one-half times as great as in the former, except for the larger values of the current. In the first case the radii of curvature of β-rays emerging from the spectrometer varied from 6.80 to 7.20 cm., in the second case from 6.80 to 7.30 cm.

In neither case could the writers find any intensity with a current of 0.39 amp. ($H = 772$ gauss), but in each case a definite intensity was obtained with a current of 0.38 amp. ($H = 759$ gauss). However, in each case with the latter current the intensities were, as far as could be determined by the writers, the same. If there were a real tail to the curve, this would not be true so that the apparent tail shown in both cases is due entirely to the finite width of the defining slits in the spectrometer. This appears to cut the axis of abscissas in the neighborhood of 0.39 amp. which corresponds to a field strength of 772 gauss, giving an end point at 6.8 cm. $\times$ 772 gauss or at $H\rho = 5250$ gauss-cm. which should be correct to 1%.

It will be realized that an apparent tail will be obtained only when the source is sufficiently strong. In an actual experiment using a source of

1/40 the intensity, the writers did not obtain such a tail, but found that if the average instead of the minimum radius of curvature was used, the same value for the end point was obtained. In this way the writers found an end point for uranium X_2 at $H\rho = 9300$ gauss-cm.

The writers' value for the end point of radium E is in fair agreement with the values reported by Madgwick (5), Alichanow, Alichanian and Dzelepow (1) and by Lyman (4), who obtained values of 5000, 5200, and 5280 gauss-cm. respectively. Of these experimenters, Lyman took the most care to determine the end point accurately, but it should be mentioned that none of them took the care the writers did to show that the tail at the end of the spectrum is due entirely to the finite range of radii of curvature permitted by the spectrometer.

The results of the writers' experiments on radium E were reported at the annual meeting of the Royal Society of Canada in May, 1936.

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THE SCATTERING OF X-RAYS AT VERY SMALL ANGLES[1]

By H. H. Penley[2] and J. A. Gray[3]

Abstract

The scattering of X-rays at small angles (minutes of arc) in commercial samples of charcoal and powdered graphite and in anthracene precipitate was investigated. In addition, the effect of pressure on the scattering in Shawinigan charcoal was determined. An absorption method, which is described, was used and the results are shown graphically in the accompanying figure.

Apparatus

A shielded filament tube of the type described by Dershem (3) was used as a source of X-rays. The target was made of copper. The rays emerged horizontally through a nickel window 0.001 in. thick. The beam was collimated by two narrow vertical platinum slits 7 cm. apart. A third slit was mounted vertically, in such a way that both its width and position on a horizontal line perpendicular to the X-ray beam could be independently adjusted. The scattering cell was placed in the collimated beam close to the second slit. For the measurements of X-ray intensity a shielded Geiger-Müller tube counter with an aluminium window was used, and this was placed just behind the third slit. The impulses were amplified and then recorded by means of a scale-of-two thyratron circuit with impulse counter. The high voltage supply was obtained from a rectifier circuit with a voltage stabilizer of the type described by Street and Johnson (9).

Discussion and Results

The apparent mass absorption coefficient, $\frac{\mu}{\rho}$, was obtained in the usual way from the equation $I = I_o\, e^{-\frac{\mu}{\rho}m}$, where I_o is the initial number of counts, I the count after the X-rays passed through the scattering material of mass m per sq. cm. The third slit was placed so that its centre coincided with that of the primary beam and for the different widths of it at which measurements were made, the angle that it subtended at the scattering material was calculated, half this angle being taken as the maximum angle of scattering of the scattered rays entering the counter. This can be only approximate for the smaller widths of the third slit owing to the finite width of the primary beam. In Fig. 1 this particular angle of scattering has been called the scattering angle and has been plotted as ordinate, μ/ρ as abscissa. It will be noticed that μ/ρ decreases as the scattering angle increases, because more scattered radiation enters the counter as the third slit is increased in width. Ultimately

μ/ρ tends to approach its true or normal value, μ_o/ρ, say. The difference $\mu/\rho - \mu_o/\rho$ may be then taken as some measure of the intensity of the radiation scattered between the angle given on the graph and large angles. In the experiments, it was found difficult to measure μ_o/ρ accurately, as in all cases I/I_o was about 0.77, so that a small error in the determination of this ratio meant a much larger error in the calculated value of the absorption coefficient.
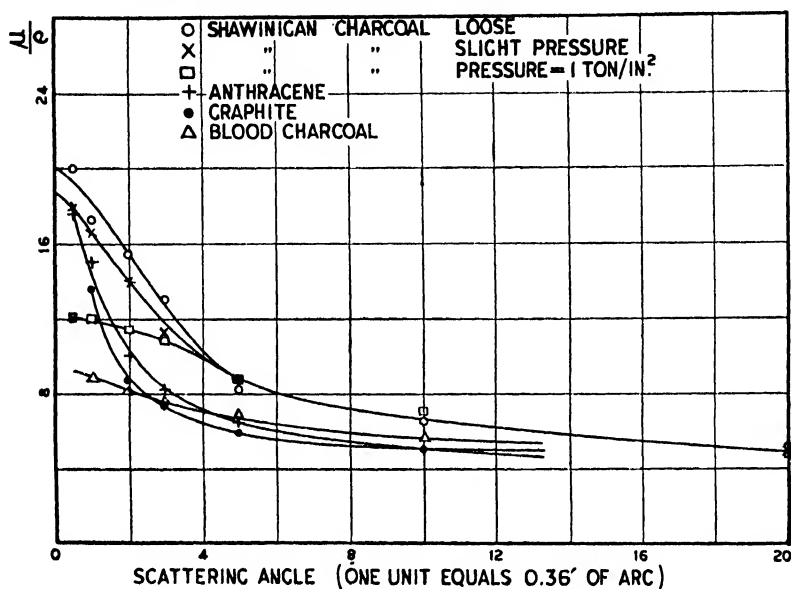
FIG. 1.

The scattering of X-rays in graphite and charcoal at small angles was reported by Gray and Zinn (5) and their work was continued in this laboratory by W. E. Bennett, who showed that there were two distinct types of scattering at small angles, one typical of charcoals and the other typical of precipitated anthracene. He showed that charcoals behave like gases of very high molecular weight, and he partially accounted for his results by a theory modelled after one given by Debye (2). He showed further that the second type of scattering could be partially explained by von Nardroff's (7) theory of the refraction and reflection of X-rays passing the small particles of the powder. Experiments on the scattering of X-rays by powders have also been carried out by Slack (8) and by Davis (1) and on charcoals by Krishnamurti (6).

The writers have tried to distinguish between the two types of scattering in these experiments. In the case of what might be called the von Nardroff scattering, the value of μ/ρ should tend to infinity as the maximum scattering angle approaches zero. This is not practicable as it would need a primary beam of zero width. If a gas is used as a scattering medium, $\dfrac{\mu}{\rho}$ tends to a maximum as the scattering angle approaches zero.

The writers' experiments confirm and extend the results of Bennett for they do show very clearly the distinction between the two types of scattering, the values of $\frac{\mu}{\rho}$ for the anthracene and graphite powder increasing markedly as the scattering angle is decreased, whereas in the charcoals $\frac{\mu}{\rho}$ does tend to increase to a maximum value. Using the Debye theory as modified by Bennett, the writers obtained a value of the order of 20 Å for the diameter of the smallest particles in the blood charcoal used, a value in agreement with that obtained by Krishnamurti (6), who used an entirely different but less exact method of dealing with the experimental results. In the Shawinigan charcoal most of the particles must be much larger. An average dimension of the particles in the anthracene precipitate that was formed by the addition of water to a solution of anthracene in ethyl alcohol and subsequent separation and drying of the precipitate was determined by use of a microscope and found to be 0.005 cm.

Three of the curves show the effect of pressure on scattering by Shawinigan charcoal at small angles. It will be noticed that the scattering at very small angles is markedly reduced by the application of pressure, but for angles greater than four minutes of arc there is no detectable change. According to theory, there should be no change in the scattering with the application of pressure if the particles are merely pushed together, while still retaining their random distribution, so that the decrease may be due to interference caused by a decrease in the randomness of the distribution or it may be due to the larger particles being broken down into smaller ones. When the particles are larger, μ/ρ is larger for zero angle of scattering and becomes equal to μ_o/ρ at a smaller angle of scattering. If one assumes it to be due entirely to the former cause, it is difficult to understand why there should be no change in the values of μ/ρ for scattering angles greater than two minutes of arc.

These experiments are being continued and it is believed that when completed they will give us further insight into the structure of substances like charcoal and artificial graphite. A full account will then be given of the work done in this laboratory by Zinn, Bennett and the writers. A brief account of the work by Bennett has been given in a note by Gray (4).

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THERMAL STRESS IN LONG CYLINDRICAL SHELLS DUE TO TEMPERATURE VARIATION ROUND THE CIRCUMFERENCE, AND THROUGH THE WALL[1]

By J. N. GOODIER[2]

Abstract

The thermal stress in thin-walled cylinders of any cross section has been investigated for internal and external temperatures each varying in any manner round the circumference but not in the axial direction. The thickness also may vary round the circumference.

A method is given for calculating the stress from given temperature distributions, whatever the shape of the cross section. The stress is evaluated for uniform, but different, inside and outside temperatures.

The circular cylinder is treated in detail and the stress found for the general case of circumferential variation. It is shown that the maximum stress will depend only on the temperature distributions and the material, and not on the thickness or diameter of the cylinder.

1. The problems of thermal stress, that is, stress due to non-uniform heating, like the ordinary problems of stress and strain in elastic bodies, fall into two groups. The first group can be satisfactorily treated only by solution of the fundamental differential equations of elasticity for appropriate boundary conditions.* The second group consists of those problems which can, for practical purposes, be adequately treated by the approximate but simple and convenient formulas of the subject usually described as the strength of materials. The well-known Bernoulli-Euler formula for the bending of beams is typical of these. The simplification arises from the circumstance of one or two. dimensions of the shapes considered—beams, thin plates, and thin shells—being small.

Some of these simple formulas will be employed to solve the problem described by the title of this paper. Temperatures varying along the axis, but not round the circumference, and temperatures uniform, but different, inside and outside a cylinder, have been dealt with by previous writers (4, 6), but only for the particular case of the circular tube. The thin tube of any shape, with completely general variation of temperature over the surfaces, presents a problem of great analytical difficulty. The differential equations involved are not linear. The same is true of the flat plate with general

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* *This group is treated in a forthcoming paper "On the integration of the thermo-elastic equations."*

surface temperatures. The restricted problem we are concerned with, however, is not only important in engineering, notably in its application to boiler tubes, but also tractable mathematically.

We begin with the incomplete cylinder, *i.e.*, the section $AQPFC$, Fig. 1, is not a closed curve. The results obtained are necessary for the complete cylinder, which, for the present, is supposed converted into an incomplete one by a cut along a generator, equivalent to a gap of zero width. The
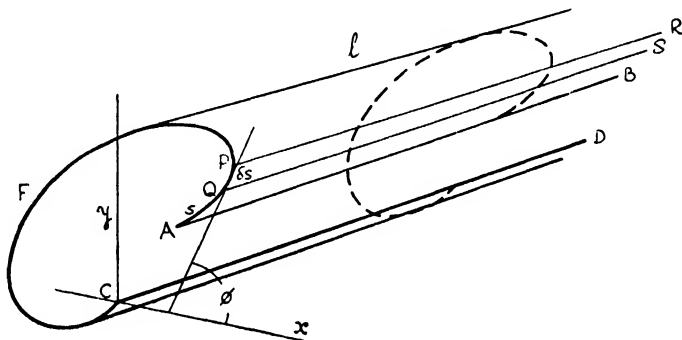
FIG. 1.

problem is reduced, by a physical argument, to the solution of a set of equations. A narrow strip $PQSR$ is considered in isolation. It is given arbitrary inside and outside temperatures, T_i and T_e respectively (the transition through the thickness being linear), while the remainder of the tube is kept unheated. The strip expands, bends and curls, and no longer fits the place from which it was taken. But by the imposition of suitable terminal forces and couples it is so far restored to its original state that it can be supposed reattached to the rest of the tube, so that points originally contiguous are so again without any necessity for straining the rest of the tube. The reassembly, however, involves relative rigid body displacements of the two cold parts PFC and QA, and hence an alteration of the gap AC. This alteration is calculated. Then the stress system required to re-close the gap AC, if the tube be a closed one, is found, and the effects of removing the imposed terminal forces and couples of the strip are considered. The effects of heating over more than an elementary strip follow by integration.

The Incomplete Cylinder

2. For the moment, let the strip $PQSR$ (Figs. 1 and 2) of (the complete) axial length l and infinitesimal arc length δs, have the inside temperature T_i, and outside temperature T_e, the rest of the cylinder being kept at temperature zero.

Let this strip be freed from the rest of the cylinder by cuts along PR and QS. Then it is free to expand, without thermal stress.* It increases its linear dimensions, and also changes its curvature on account of the tem-

* There is a general theorem that temperature distributions linear in cartesian co-ordinates give rise to no stress (8, p. 204).

perature gradient through the thickness. If the mean temperature $T_m = \frac{1}{2}(T_i + T_e)$, then the length increases by a uniform linear strain αT_m, *i.e.*, by $l\alpha T_m$, α being the coefficient of linear expansion. The arc length δs increases by $\delta s \cdot \alpha T_m$. The thickness h increases by $h\alpha T_m$. The length l, which originally had no curvature, becomes curved, as sketched in Fig. 2 (with $T_e > T_i$), to a radius r, where $1/r = (T_e - T_i)\alpha/h$.
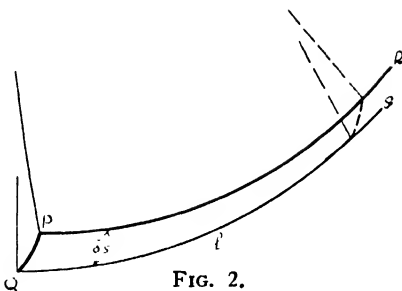
FIG. 2.

The arc δs changes its curvature by the same amount.

3. A compressive stress $E\alpha T_m$, applied to the ends of the strip will exactly cancel the thermal strain αT_m in the direction l (where E is Young's modulus). It will increase δs by a strain $\sigma\alpha T_m$ (where σ is Poisson's ratio) so that the total increase of δs becomes $\delta s(1 + \sigma)\alpha T_m$. It will also increase the thickness h by $h\sigma\alpha T_m$.

A bending moment of suitable magnitude, applied to the ends, will exactly cancel the thermal curvature of l, $(T_e - T_i)\alpha/h$. It is easily found from simple beam formulas that the necessary bending moment is $\frac{1}{12}E\alpha h^2(T_e - T_i)\delta s$. The vector representing this moment is in the direction of δs.

This moment will produce an *anticlastic* curvature of δs, of amount $\sigma(T_e - T_i)\alpha/h$, and the total change of curvature of δs is therefore now $(1 + \sigma)(T_e - T_i)\alpha/h$.

The edges PR and QS of the strip are at present thicker than the thickness h of the cold tube by $h(1 + \sigma)\alpha T_m$. In order to bring the faces of the cuts of the strip and of the rest of the tube to the same configuration, it must be supposed that shearing and normal tractions as indicated in Fig. 3, and perhaps others, act on the strip, and equal and opposite tractions on the rest of the tube.
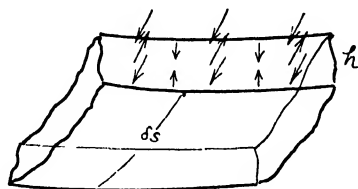
FIG. 3.

It is however neither practicable nor necessary to compute these tractions and their effects. The strip, at present, is regarded as hot, and the rest of the tube as cold. But later the effects of heating all such strips will be added so as to arrive at a tube heated all round, the temperature varying smoothly. Evidently the adjustment of the thickness of one strip to that of its neighbors involves only the temperature differentials. In the limit, therefore, the required tractions on the cuts such as PR and QS will vanish. We may say that they disappear in the process of integration.*

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* *The validity of this argument may be better seen by considering a problem of plane stress. Let a long strip be compressed on finite opposite segments on the two edges. The part between these segments may be considered in isolation, and we may inquire what tractions are necessary to fit it back into the strip. We should find that an adjustment of thickness is required, just as in the present problem. But if the compressive forces have a smooth distribution over a succession of infinitesimal segments, the process of integration involved eliminates the tractions that have to be introduced to adjust the thickness, and the stress is plane. This is confirmed by the exact analytical solution of the plane stress problem.*

4. For the present, suppose that the tractions act, so that the thicknesses become equal. Any other possible effects due to the tractions on the strip need not be considered. Then we may suppose that the strip is rejoined to the other two parts of the cylinder. But on account of the alterations in the length and curvature of δs, these parts will no longer have their former relative positions.

Consider any cross section of the cylinder and draw rectangular axes Cx, Cy with origin on CD. In Fig. 1 these are drawn on the end $AQPFC$, for convenience.

Then the displacement of AQ relative to CFP has x and y components given by,

$$-(1 + \sigma)\alpha T_m \cos \phi \,.\, \delta s - (1 + \sigma)\alpha(T_e - T_i)\frac{y}{h}\delta s$$

and

$$-(1 + \sigma)\alpha T_m \sin \phi \,.\, \delta s + (1 + \sigma)\alpha(T_e - T_i)\frac{x}{h}\delta s \,.$$

The first terms arise from the extension of δs, the second terms from the change in its curvature; the rotation (anticlockwise) of AQ relative to CFP is $-(1 + \sigma)\alpha(T_e - T_i)h^{-1}\delta s$; x and y are the co-ordinates of δs, and ϕ is the angle δs makes with the x-axis.

5. If now all the other strips into which the cylinder may be divided are treated in the same way, each being given its proper temperatures, the displacements δ_x and δ_y and rotation ω of the edge AB relative to the edge CD may be obtained by superposition. Then

$$\left.\begin{aligned}
\delta_x &= -(1 + \sigma)\alpha\int T_m \cos \phi \,.\, ds - (1 + \sigma)\alpha\int (T_e - T_i)\frac{y}{h}ds \,, \\[2mm]
\delta_y &= -(1 + \sigma)\alpha\int T_m \sin \phi \,.\, ds + (1 + \sigma)\alpha\int (T_e - T_i)\frac{x}{h}ds \,, \\[2mm]
\omega &= -(1 + \sigma)\alpha\int (T_e - T_i)\frac{ds}{h} \,,
\end{aligned}\right\} \quad (1)$$

T_m, T_e and T_i being now given functions of s, the arc length. The integrals are taken all round the section.

These displacements and rotation are maintained by the temperature distribution together with:

(i) Stress $-E\alpha T_m$ on the ends of the cylinder;

(ii) A distribution of moment on the ends,

$$m = \tfrac{1}{12}E\alpha h^2(T_e - T_i),$$

per unit length of arc, the vector of m being directed along δs or along the tangent at any point of the end section.

The state of stress anywhere in the wall of the cylinder is given by the same stress and moment. There is no stress other than the axial component.

6. The end stresses (i) and (ii) of Art. 5 may be eliminated by superposing the ordinary isothermal stress distribution having equal and opposite end stress and moment. The complete determination of this distribution is a problem in the theory of thin shells. However, if the cylinder is long, the distribution in the middle part will depend, according to the Principle of Saint-Venant, only on the *resultant* force and couple on the ends. The resultant force is $E\alpha\int hT_m\,ds$ and the resultant couple has components

$$\left.\begin{array}{l} M_x = -\tfrac{1}{12}E\alpha\int h^2(T_e - T_i)\cos\phi\,.\,ds\,, \\ M_y = -\tfrac{1}{12}E\alpha\int h^2(T_e - T_i)\sin\phi\,.\,ds\,, \end{array}\right\} \qquad (2)$$

and from these the corresponding stress in the middle part can be found from the simple beam theory.

The Complete Cylinder

7. If a cut is made along a generator, the formulas (1) give the displacement and rotation of one face of the cut relative to the other, when the end actions (i) and (ii) of Art. 5 are applied, and the cylinder is heated. The integrals are now taken around the circumference.

The faces of the cut may be brought together by a suitable force and couple on one face, an equal and opposite force and couple on the other face, and rejoined. This introduces an additional stress distribution to be superposed on that of Art. 5.

To evaluate it, consider the forces X_o and Y_o and moment M_o, per unit axial length, distributed uniformly along the faces of the cut, acting on the cut tube (Fig. 4). The displacements and rotation of the face A relative to the face C are conveniently found by Castigliano's theorem (7, p. 434). Since we are dealing with a cylinder and not a ring, we use the plate modulus* $E/(1 - \sigma^2)$ instead of Young's modulus, E, and write D for $Eh^3/12(1 - \sigma^2)$. The thickness h will now be taken as constant, although there would be no difficulty in retaining it as a variable. Then,
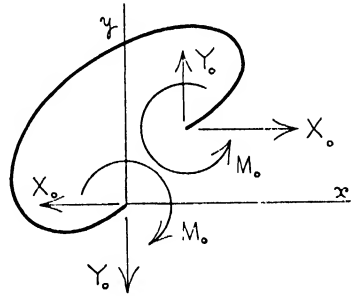
FIG. 4.

$$\left.\begin{array}{l} D\delta_x = M_o\int yds + X_o\int y^2ds - Y_o\int xyds \\ D\delta_y = -M_o\int xds - X_o\int xyds + Y_o\int x^2ds \\ D\omega = M_o\int ds + X_o\int yds - Y_o\int xds \end{array}\right\} \qquad (3)$$

The integrals can be expressed in terms of the mean circumference of the section, L, the co-ordinates of the centroid $\bar{x}$, $\bar{y}$, the moments of inertia I_{xx}, I_{yy}, and the product of inertia I_{xy}, of the area of the section, since $L = \int ds$, $L\bar{x} = \int xds$, $L\bar{y} = \int yds$, and $I_{xx} = h\int y^2ds$, $I_{yy} = h\int x^2ds$, $I_{xy} = h\int xyds$. The displacements and rotation given by Equations (3) must be equal and opposite

* *Expressing the effect of preventing anticlastic curvature.*

to the displacements and rotation given by Equations (1). The forces X_o and Y_o and the couple M_o can be found by solving the equations,

$$
\left.
\begin{aligned}
M_o L h \bar{y} + X_o I_{xx} - Y_o I_{xy} &= D(1+\sigma)\alpha[h\!\int T_m \cos\phi \,.\, ds + \int(T_e - T_i)y\,ds], \\
-M_o L h \bar{x} - X_o I_{xy} + Y_o I_{yy} &= D(1+\sigma)\alpha[h\!\int T_m \sin\phi \,.\, ds - \int(T_e - T_i)x\,ds], \\
(M_o + X_o \bar{y} - Y_o \bar{x})Lh &= D(1+\sigma)\alpha\!\int(T_e - T_i)ds \,.
\end{aligned}
\right\}(4)
$$

8. The axial stress is made up of four contributions:

(i) A stress $-E\alpha T_m$ (Art. 3);

(ii) A stress corresponding to the distribution of an axial bending moment $\frac{1}{12}E\alpha h^2(T_e - T_i)$ per unit arc length on the mean circumference (Art. 3);

(iii) The axial stress due to the distribution of traction $E\alpha T_m$ on the *ends*. This cancels, on the ends only, the stress (i);

(iv) The axial stress due to the distribution of the couple on the *ends* $-\frac{1}{12}E\alpha h^2(T_e - T_i)$ per unit arc length on the mean circumference. This cancels, on the ends only, the stress (iii).

The ends are then completely free.

The resultant moments of (iv) are given by Equations (2), and the stress due to them, in the middle part, *i.e.*, away from the ends, can be calculated by the simple beam formulas. The appropriate moments of inertia are not I_{xx} and I_{yy} as defined previously, since the latter are referred to axes not through the centroid of the section. Writing I'_{xx}, I'_{yy} for the centroidal moments of inertia, and ζ for the distance normal to the middle surface measured inwards, the stresses (i) to (iv) may be combined into the complete expression for the axial stress

$$
\begin{aligned}
E\alpha\Bigg[-T_m + \frac{\zeta}{h}(T_e - T_i) + \frac{1}{L}\!\int T_m ds \\
+ \frac{h^2(x - \bar{x})}{12I'_{xx}}\!\int(T_e - T_i)\sin\phi \,.\, ds - \frac{h^2(y - \bar{y})}{12I'_{yy}}\!\int(T_e - T_i)\cos\phi \,.\, ds \Bigg] (5)
\end{aligned}
$$

When the shape of the cylinder, and the temperature distributions, are given, it is a straightforward process to evaluate the coefficients in Equations (4), analytically or graphically, and to solve for X_o, Y_o and M_o, and from these compute the corresponding stress. The axial stress can be found directly from Expression (5).

Simple formulas can be derived for circular, elliptical, rectangular or other regular sections. The further development, with the exception of the next paragraph, will be confined to the circular case.

Cylinder of Any Shape, but of Uniform Thickness, with Uniform but Unequal Inside and Outside Temperatures

9. It is evident that since the temperature difference is constant around the cylinder, the curvature changes due to it in conjunction with the auxiliary end forces and couples will also be constant around the cylinder. Such a

curvature change can be annulled by a moment distribution M_o. Clearly this is what is required to close the gap. It is easily found that

$$M_o = \frac{\alpha}{h} D(1 + \sigma)(T_e - T_i) .$$

The extreme circumferential stress $(6M_o/h^2)$, then, has the values*

$$\pm \frac{E\alpha(T_e - T_i)}{2(1 - \sigma)} .$$

The complete axial stress is given by (ii) of Art 8, and has the extreme values

$$\pm \tfrac{1}{2} E\alpha(T_e - T_i)$$

except near the ends, which, of course, are free of traction. It is noteworthy that these values are independent of the size, shape and thickness of the cylinder, depending only on the material and the temperatures occurring within it.

It is known that these formulas hold for the special case of the circular tube (8, p. 373).

The Circular Cylinder

10. When the cylinder has a mean radius a, the expressions on the left of the Equations (4) reduce to $\pi a^2 h(2M_o + 3aX_o)$, $\pi a^3 h Y_o$, $2\pi a(M_o + aX_o)$ respectively, with axes as in Fig. 5; in the integrals on the right, ds is replaced by $a\,d\phi$, x by $a \sin \phi$, and y by $a(1 - \cos \phi)$. The solution of the equations is
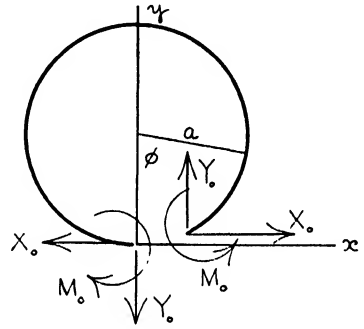
FIG. 5.

$$X_o = \frac{D}{\pi a^2} (1 + \sigma)\alpha \left[\int_0^{2\pi} T_m \cos \phi \, d\phi - \frac{a}{h} \int_0^{2\pi} (T_e - T_i) \cos \phi \, d\phi \right] ,$$

$$Y_o = \frac{D}{\pi a^2} (1 + \sigma)\alpha \left[\int_0^{2\pi} T_m \sin \phi \, d\phi - \frac{a}{h} \int_0^{2\pi} (T_e - T_i) \sin \phi \, d\phi \right] , \qquad (6)$$

$$M_o = \frac{D}{\pi a} (1 + \sigma)\alpha \left[-\int_0^{2\pi} T_m \cos \phi \, d\phi + \frac{a}{2h} \int_0^{2\pi} (T_e - T_i)(1 + 2 \cos \phi) d\phi \right] .$$

These formulas will give the bending moment, $M_o + X_o y - Y_o x$, per unit axial length, explicitly in terms of the given temperature distributions. The direct stress due to X_o and Y_o will be small, of the order h/a, in comparison with the bending stress.

When the temperature difference $T_e - T_i$ is as great as or greater than the mean temperature $T_m = \tfrac{1}{2}(T_e + T_i)$, the contributions from the latter will be negligible, being of the order h/a, compared with the contributions arising from the temperature difference.

* *Positive signs pertain to the inside.*

11. The integrals occurring in Expression (6) may be replaced by coefficients in the Fourier expansion of T_e and T_i. Let

$$T_e = A_0 + A_1 \cos \phi + A_2 \cos 2\phi + \cdots$$
$$+ B_1 \sin \phi + B_2 \sin 2\phi + \cdots$$
$$T_i = A_0' + A_1' \cos \phi + A_2' \cos 2\phi + \cdots$$
$$+ B_1' \sin \phi + B_2' \sin 2\phi + \cdots$$

Then

$$2\pi A_0 = \int_0^{2\pi} T_e \, d\phi, \quad \pi A_1 = \int_0^{2\pi} T_e \cos \phi \, d\phi, \quad \pi B_1 = \int_0^{2\pi} T_e \sin \phi \, d\phi$$

and A_0', A_1', B_1' are similarly expressed in terms of T_i.

Thus X_o, Y_o and M_o, and the stresses corresponding to them, are independent of the terms in $\cos 2\phi$, $\sin 2\phi$, and all higher harmonics of the temperatures.

Replacing the factors $\frac{a}{h} \pm \frac{1}{2}$ by $\frac{a}{h}$, Equations (6) can be written,

$$\left. \begin{aligned} X_o &= -\frac{D}{ah}(1 + \sigma)\alpha(A_1 - A_1'), \\ Y_o &= -\frac{D}{ah}(1 + \sigma)\alpha(B_1 - B_1'), \\ M_o &= \frac{D}{h}(1 + \sigma)\alpha[A_1 - A_1' + A_0 - A_0']. \end{aligned} \right\} \quad (7)$$

To obtain the corresponding extreme fibre stress, neglecting the direct stress due to X_o and Y_o, the moment $M = M_o + X_o y - Y_o x$ is multiplied by $6/h^2$. The result is

$$\pm \frac{E\alpha}{2(1 - \sigma)} \left\{ A_0 - A_0' + (A_1 - A_1') \cos \phi + (B_1 - B_1') \sin \phi \right\} \quad (8)$$

whence the maximum follows easily. This is independent of the radius and thickness of the cylinder.

The complete expression for the axial stress at the middle part of the length is

$$E\alpha \left\{ -T_m + \frac{\zeta}{h}(T_e - T_i) + \tfrac{1}{2}(A_0 + A_0') \right.$$
$$\left. + (A_1 - A_1') \frac{h}{12a} \cos \phi + (B_1 - B_1') \frac{h}{12a} \sin \phi \right\}. \quad (9)$$

The last two terms will be relatively small. When they are neglected this stress becomes independent of a and h.
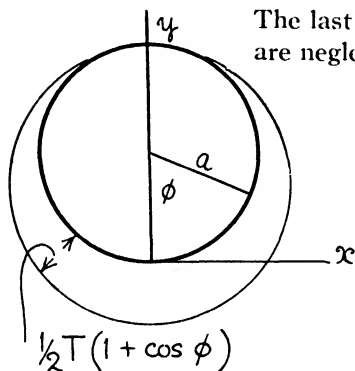
12. As an example of thermal stress in a circular cylinder, let the internal temperature be uniform, and let the external temperature exceed the internal by $\frac{1}{2}T(1 + \cos \phi)$. Then T is the maximum temperature difference, and the distribution of temperature difference round the circumference is as indicated by the polar diagram, Fig. 6. It corresponds roughly to a tube heated from below, and containing a well mixed fluid.

Fig. 6.

A_0 and A_1 are each equal to $\frac{1}{2}T$, and all other Fourier coefficients are zero. Then

$$X_o = -\frac{D}{ah}(1 + \sigma)\alpha\frac{T}{2}, \quad Y_o = 0, \text{ and } M_o = \frac{D}{h}(1 + \sigma)\alpha T .$$

The moment M is given by

$$\frac{D}{h}(1 + \sigma)\alpha T\left(1 - \frac{y}{2a}\right) .$$

The maximum is at $y = 0$, and corresponds to an extreme fibre stress

$$\pm E\alpha T/2(1 - \sigma).$$

To obtain a numerical result, take the internal temperature as 100° C., the maximum external temperature as 200° C., E as 3×10^7 lb. per sq. in., α as 11.6×10^{-6} per °C., σ as 0.3 (as for steel). Then $E\alpha T/2(1 - \sigma)$ is nearly equal to 25,000 lb. per sq. in.

The axial stress can be found from Expression (9). With the assumed distribution, there is a compressive stress in the hottest part ($\phi = y = \text{o}$) nearly equal to $\frac{3}{4}E\alpha T$, or 27,000 lb. per sq. in. for the values taken. This is the value for the stress at the inside. At the outside, the axial stress is 9,000 lb. per sq. in. tension.

13. As a final example, let the outside of the cylinder be heated to a temperature T, kept constant over a small arc of circumferential length λ, and let the rest of the outside surface* and the whole inside surface be kept at zero temperature. This is a rough representation of a distribution that might occur in a welding process.

It is easily shown that the maximum circumferential stress is given by

$$\frac{3}{4}\frac{E\alpha T}{1 - \sigma} \cdot \frac{\lambda}{a} .$$

Since this is proportional to λ/a, it shows that localized heating does not produce large circumferential stresses. This is true, of course, only while there is no *axial* variation of temperature.

As to the axial stress under such conditions, the parts (i) and (ii) of Art. 8 are confined to the heated strip and occur throughout its length: (iii) and (iv) are distributions due to forces and moments localized on the ends of the heated strip. In the interior these will set up only very small stresses. In the interior, therefore, there will be an axial stress, given by $-\frac{1}{2}E\alpha T(1 \pm 2\zeta/h)$, confined to the heated strip, or a compressive stress varying from zero at the inside to $E\alpha T$ at the outside.

The stress at the ends of the cylinder presents a separate problem, and can be dealt with approximately by methods given in another paper (2). It may

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* *This disregard of the restriction to smooth temperature variations, referred to in Art. 3, is of no more importance here than its equivalent in plane stress systems with discontinuous boundary stress. The discontinuity conveniently replaces a variation as abrupt as is allowed, without seriously affecting the conclusions.*

be shown that there would be local tensile circumferential stresses at the ends with a maximum value $2E\alpha T/(3 + \sigma)$.

14. The thermal stress in a *thick* cylinder with a steady-state temperature distribution due to surface temperatures arbitrarily distributed round the inside and outside surfaces, but independent of the axial co-ordinate, can be reduced, as was shown by N. Muscheliŝvili (5) and M. A. Biot (1), to an axial stress, and a dislocational stress corresponding to the stress specified above by means of X_o, Y_o and M_o. In order to find the appropriate magnitudes of the dislocations it is necessary first to obtain the solution of the potential problem of finding the temperature distribution from the surface temperatures.

By restricting the investigation described in this paper to the thin cylinder, the potential problem is avoided, and it becomes possible to find the stress and strain in terms of arbitrarily given surface temperatures for a cylinder of any shape and variable thickness. It should be said, however, that the potential problem presents no difficulties in the particular case of the uniform, thick circular cylinder. Explicit formulas for this case are given in another paper (3).

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THE SPECIFIC HEAT OF COPPER FROM 30° TO 200° K.[1]

By S. M. DOCKERTY[2]

Abstract

An all-metal adiabatic vacuum calorimeter was used to determine the specific heat of copper over small temperature intervals from 30° to 200° K. The accuracy is considered to be within 0.05% for the greater part of the range. A curve is given showing the variation with temperature of the characteristic temperature, θ, for copper.

Introduction

Bronson, Chisholm, and Dockerty (2, 4) described the development of an all-metal adiabatic calorimeter and its use in precision measurements of the specific heat of copper from −80° to 100° C. The present paper deals with the construction of a similar type of calorimeter for much lower temperatures, used to determine the specific heat of copper from 30° to 200° K.

The method, that of electrical heating under adiabatic conditions, has also been described (2, 4). The general features can be seen from the diagram of the apparatus in Fig. 1. The calorimeter is cooled down to the lowest
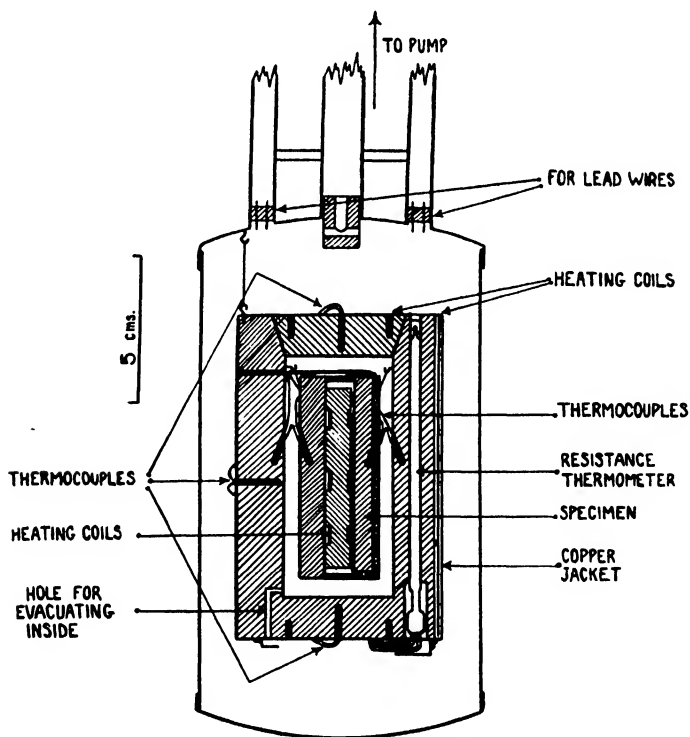
FIG. 1. *Adiabatic calorimeter.*

point of the range at which one wishes to work, by immersing the container in a low temperature bath, the rate of cooling being speeded up somewhat by having hydrogen gas in the container.

When the desired temperature is reached the container is evacuated. The specimen is heated so as to change its temperature in steps of 5° to 8°, the times of heating varying from 15 to 25 min. Adiabatic conditions are obtained by keeping the temperature of the jacket as nearly as possible equal to that of the specimen, as indicated by the differential thermocouples. The temperatures are so adjusted, before and after the heating period, that the differences between the jacket and the specimen are less than 0.001° C. Thus the temperature of the jacket, as measured by the resistance thermometers, will be also the temperature of the specimen. The electrical energy supplied was measured, to within 0.02%, with a potentiometer and a standard cell that was recently calibrated in the laboratories of the National Research Council of Canada. The mass of the specimen was known to within 0.01%. Temperature differences were measured to within 0.02% for the greater part of the range, the precision being somewhat less than this at low temperatures.

Apparatus

Jacket

Some difficulty was experienced with temperature gradients in the jacket of the older apparatus owing to the faulty distribution of heat loss. This was largely avoided in the present apparatus by using pure copper for the jacket, and by high evacuation which increased the thermal resistance between the jacket and the container about five times. Temperature gradients that were due to non-uniform heating were eliminated as before by winding separate heating coils on the sides and ends of the jacket; because of the high vacuum it was necessary to cement these coils in deep grooves.

Differential thermocouples between the sides and ends of the jacket, as shown in Fig. 1, served to indicate temperature inequalities over the inner surface. These were put in from the outside and were left in permanently, so that adjustments could be made during the actual experiments.

Two jackets were made by machining a 3-in. bar of copper. The first, which was used for most of the measurements above liquid air temperature, was about one and one-half times as large as that shown in Fig. 1, and differed from it in that it was divided horizontally at the centre into two symmetrical sections. This feature proved somewhat troublesome because it was found difficult to keep both sections at the same temperature. This equality was necessary because the resistance thermometers would indicate the temperature of the section in which their coils were situated. In addition, it was found that, because of the high vacuum, the size could be reduced considerably without affecting the accuracy of the results; this feature was desirable for the cooling to liquid hydrogen temperatures. A new jacket was therefore made as shown in Fig. 1. Care was taken to keep the end plug at the same temperature as the rest of the jacket, but a slight difference

would have no serious effect. Small leads of copper wire were used to prevent the production of cold spots on the jackets at low temperatures where the thermal conductivity of copper becomes quite high.

Copper Specimen

This consisted of a bar of commercially pure cold-rolled copper, a copper plug, and an 80-ohm manganin heating coil fitted together as shown in Fig. 1. The weights of the specimens used with the large and small jackets were about 650 and 320 gm. respectively. The amount of foreign material such as silk insulation, silk suspension, cement, and shellac was reduced to less than 0.1% of the total copper equivalent.

Because of the high vacuum it was necessary to bind the heating coil to the plug with a thin coat of shellac. Small copper leads were used, and care was taken that these should be in good thermal contact with both the specimen and the jacket.

The two-junction copper-constantan thermocouples were cemented in small holes in the specimen and the jacket respectively as shown. With a sensitive galvanometer these thermocouples would indicate temperature differences between the specimen and the jacket of less than 0.001° C.

Resistance Thermometers

Temperatures were measured with metal-stem resistance thermometers of platinum and lead placed in holes bored lengthwise in the jacket. To prevent heating and lagging effects it was necessary that the thermometers should not be evacuated with the rest of the system. They were therefore filled with helium gas at a pressure of one atmosphere, and sealed. A very satisfactory type of seal, which holds at low temperatures, is shown in Fig. 2.

Resistances were measured with a carefully calibrated Müller bridge maintained at a constant temperature in a thermostatic box. Small copper wire leads were used and inequalities in compensation were balanced out by a method involving two readings on the bridge (7).

The platinum coil was made of 0.002 in. wire ($r_0 = 30$ ohms) obtained from Johnson-Matthey, with a specified value for δ (Equation (1)) of 1.49. The lead coil was of 0.003 in. extruded wire ($r_0 = 9$ ohms) obtained from the Baker Chemical Company, and was rated of high purity.

The platinum thermometer was calibrated in ice, steam, liquid oxygen, liquid hydrogen, and liquid helium in the usual way. The last two points proved to be of no interest from the point of view of calibration. In addition, a careful calibration was made between $-183°$ C. and $-210°$ C. by means
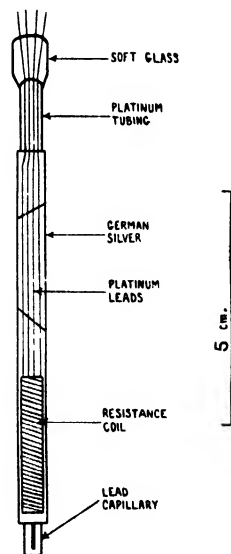
FIG. 2.
Resistance thermometer.

of an oxygen vapor pressure thermometer. Pure gas was obtained for this purpose by heating potassium permanganate in a vacuum.

The values of the resistance ratio $\left(R = \dfrac{r}{r_0}\right)$ obtained for the various temperatures are given in Table I. Repeated calibrations at some of these points showed no noticeable change over a period of a year.

TABLE I

RESISTANCE RATIO FOR PLATINUM THERMOMETER

Temp., °C.	R	Temp., °C.	R
100.00	1.38976	−191.01	0.21407
0.00	1.00000	−195.73	0.19377
−182.98	0.24891	−210.41	0.13152
−187.76	0.22823	−252.78	0.00957
−188.66	0.22434	−269.0	0.00438

The lead thermometer was calibrated in ice and in liquid hydrogen, and indirectly for the range −180° to −210° C. by comparison with the platinum thermometer during the actual experiments. A slight zero shift was observed after the thermometer had been immersed in liquid air or in liquid hydrogen. The values of R obtained for the oxygen and hydrogen points were 0.29725 at −182.98° C. and 0.03615 at −252.78° C.

Resistance of Platinum. The international Temperature Scale (3) is defined in terms of the platinum resistance thermometer by the equation,

$$t - t_{pt} = \delta \left(\frac{t^2}{100^2} - \frac{t}{100} \right) + \gamma (t - 100) t^3 , \qquad (1)$$

for $0° > t > - 193°$ C. However, it has been found by Heuse and Otto (10), and by Keesom and Dammers (11), that temperatures derived by means of Equation (1) depart from the thermodynamic scale by as much as 0.05° C. at −80° C. and −140° C., and in opposite directions.

Henning (9) has deduced that the resistances of different specimens of platinum should satisfy the relation,

$$\Delta R = a(R - 1) + b(R - 1)^2 , \qquad (2)$$

where R is the resistance ratio r/r_0. Onnes (13) has shown that this relation holds to −215° C. with an accuracy in the derived temperatures of 0.02° C. Below this temperature no satisfactory relation has been found for comparing the resistances of different samples.

Temperatures were calculated directly by means of equation (1) from the resistance measurements of the platinum thermometer, and also by comparison with a detailed standard calibration by means of Equation (2). The standards used were Henning's thermometer No. 29 to −195° C., and Onnes' No. 23' from −195° to −210° C., the values of R for the standards being taken from

Leiden Comm. Supp. 58. Temperatures calculated by the two methods differed at some points by as much as 0.06° C. This gave rise to differences of as much as 0.1% in the temperature intervals. This is in agreement with the results of Heuse and Otto, and Keesom and Dammers. The method of comparison by Equation (2) was found to give close agreement with the calibration by means of the oxygen vapor pressure thermometer. The latter method was therefore adopted for the calculation of temperatures to −210° C.

Resistance of Lead. It has generally been found that the resistance ratios R, R', of different specimens of lead can be compared by means of the relation,

$$R' = \frac{R - a}{1 - a},$$

which reduces to

$$\Delta R = a(R - 1). \tag{3}$$

Temperatures were first calculated by means of Equation (3), using as a standard a specimen calibrated in detail by Onnes (5) and deriving the constant a from the resistance at the hydrogen point. This method gave only approximate agreement with the calibration points at higher temperatures, and consequently the same Equation (2) that was used for platinum was also adopted for lead, with the constants a and b determined from the hydrogen and oxygen points. A further small correction term was added to allow for a discrepancy of 0.04° at −210° C.

Experimental Measurements

To test the reliability of the calorimeter under widely different experimental conditions some determinations of the specific heat, with the copper specimen above room temperature, were made; *(A)* with the calorimeter in a water bath, and *(B)* in a bath of liquid air. With the large calorimeter the values obtained from *(B)* were 0.15% higher than those from *(A)*. In view of a similar correction in the previous investigation (4) it was thought that, with a liquid air bath, the correction would be proportional to the heat loss from the jacket. . The measurements at temperatures above that of liquid air were made with this calorimeter. However, it was feared that at liquid hydrogen temperatures, where the heat capacity of copper is low, the above correction might have a larger value, and therefore the smaller calorimeter was constructed for use in the lower temperature region. Results obtained above room temperature with this new calorimeter for Cases *(A)* and *(B)* agreed within 0.02% of each other and within 0.05% of those obtained with the large calorimeter for Case *(A)*. It was found that, when the differential thermocouples were kept balanced, the temperature of the specimen did not change by more than 0.001° C. in one hour.

Measurements were made with the small calorimeter from 30° to 90° K. and two determinations were made at 93° K. and 133° K. At both these temperatures the results were 0.15% lower than those obtained with the large calorimeter. This showed that the correction factor did not vary as first supposed but was constant to 90° K.

Table II gives the values obtained for the specific heat of copper from 30° to 200° K. Temperatures are given in the Kelvin scale (0° C. = 273.15° K.). The value of C_p is given in joules per gram and in calories per mole (1 Cal.$_{15°}$ = 4.1835 electrical joules). The values of C_v are calculated from the relation

$$C_p - C_v = 1.60 \times 10^{-5} C_p{}^2 T.$$

The values of the characteristic temperature, θ, were found from a table of Debye functions given by Beattie (1). A value of 5.9613 calories per mole was used for $3R$.

Since some of the temperature intervals were as great as 8° C., calculations were made to find the difference between the mean specific heat over the range in question and the true specific heat at the mean temperature. For all except the two lowest points the difference proved to be within the limits of experimental error. For the first and second points however the correction amounted to about 1%. This correction was quite accurately determined by a graphical method.

TABLE II
THE SPECIFIC HEAT OF COPPER

Temp., °K.	C_p Joules per gm.	C_p Cal. per mole	$C_p - C_v$ Cal. per mole	C_v Cal. per mole	θ
28.64	0.02280	0.3475	0.0002	0.3473	314.0
35.93	0.04440	0.6745	0.0005	0.6740	310.5
42.58	0.06985	1.047	0.001	1.046	309.1
50.13	0.09855	1.497	0.002	1.495	309.5
59.24	0.1339	2.035	0.004	2.031	310.7
67.21	0.1620	2.462	0.007	2.455	312.7
74.64	0.1870	2.840	0.009	2.831	312.9
87.45	0.2239	3.402	0.016	3.386	313.0
87.88	0.2249	3.417	0.016	3.401	313.2
92.79	0.2365	3.594	0.019	3.575	313.8
93.18	0.2373	3.606	0.019	3.587	314.0
97.41	0.2463	3.743	0.022	3.721	314.9
103.08	0.2579	3.919	0.025	3.894	315.1
108.51	0.2681	4.074	0.029	4.045	315.3
113.73	0.2772	4.212	0.032	4.180	314.9
119.38	0.2861	4.347	0.036	4.311	314.9
125.42	0.2947	4.467	0.040	4.438	314.6
131.29	0.3025	4.597	0.044	4.553	313.9
132.97	0.3043	4.624	0.045	4.579	314.4
137.48	0.3092	4.699	0.049	4.650	314.8
144.24	0.3171	4.818	0.054	4.764	312.9
151.08	0.3236	4.917	0.058	4.859	312.3
157.79	0.3293	5.004	0.063	4.941	312.0
164.71	0.3345	5.083	0.068	5.015	312.0
171.83	0.3399	5.165	0.073	5.092	310.4
178.84	0.3443	5.232	0.078	5.154	309.9
186.33	0.3486	5.297	0.084	5.213	309.6
194.29	0.3528	5.361	0.089	5.272	308.6

Discussion of Results

The accuracy of the results is limited in general by that of the temperature measurements. Above 80° K. it is considered to be within 0.05%. Below this temperature the accuracy is somewhat reduced because of uncertainties in the use of the lead thermometer. An error of more than 0.01° in a 5° interval in this range is considered unlikely.

Fig. 3 gives the values of θ plotted against the temperature. The corresponding values for the specific heat can be found from Beattie's table. Above 90° K. only one point lies off the curve by an amount corresponding to more than 0.05% in C_p. The rise in the curve at 70° K. corresponds to about 0.3% in C_p and is thought to be well within the limits of error. The existence
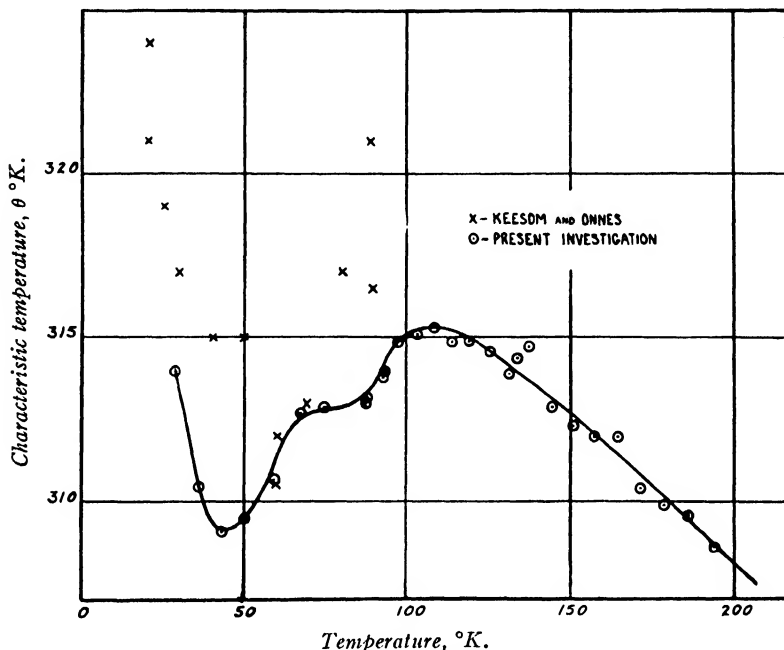
Fig. 3. *Characteristic temperature, θ, for copper.*

of a minimum at about 50° K. is in fair agreement with the work of Keesom and Onnes (12). Their points show a maximum deviation from the present curve of about 3%, which was the accuracy they had claimed. Both show an increase in the value of θ at lower temperatures.

Above 110° K. the curve falls quite rapidly. In the previous work above 200° K. it was found that the specific heat curve could be fitted with a constant value of θ if a term, linear with the temperature, were added to Debye's equation. This equation was found to hold, in the present case, to 100° K. with an accuracy of 1%. Below this temperature however the equation failed, since it amounted roughly to a linear correction in θ.

The results agree with those of Griffiths and Griffiths (8) at room temperature but fall below their curve by 4% at 140° K. The results agree however at this temperature with the results of Eucken and Werth (6).

In the previous work (2, 4) differences of 0.2% were found in the specific heat of specimens of specific gravities 8.8 and 8.9. The specific gravity of the specimen used in the previous work from −78° to 0° C. was 8.90, while that of the specimen used in the present work was 8.91. The two should have specific heats very nearly equal. Later unpublished work has shown

that the values previously obtained (4) are too low by 0.2%. When this correction is made the two agree to within 0.05%, both at room temperature and at 200° K.

Acknowledgments

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THE MEASUREMENT OF EXTRA HARD X-RAYS AND GAMMA RAYS IN ROENTGENS[1]

BY G. C. LAURENCE[2]

Abstract

The intensity in roentgens per second of X-rays or γ-rays harder than 0.03Å may be measured with a small thimble chamber with homogeneous walls of elements below atomic number 13 and thick enough to be impermeable to the fastest secondary β-rays. The ionization current measured under saturation conditions at standard temperature and pressure is divided by BV, and correction is made for the apparent absorption of the X-rays in the walls. V is the volume of the chamber and B is given by

$$B = 1 + 2 \log_e (Z_w/Z_a) \, J/L + [2 \log_e (Z_w/Z_a)]^2 \, K/L + \cdots$$

A table (Table IV) of the values of $2 \log_e (Z_w/Z_a)$ for different wall materials is given, and J, K, and L are plotted (Fig. 2) as functions of the quality of the radiation.

The absolute intensity of radiation in quanta per square centimetre per second may be obtained from

$$c = BL \times 2.92 \times 10^{15} \text{ e.s.u. per cc.,}$$

in which c is the ionization current per unit volume in the chamber, at standard temperature and pressure, produced by one quantum per square centimetre per second.

The intensity of the radiation from one milligram of radium in equilibrium, and covered by platinum of wall thickness t, at one centimetre distance is $(8.9_8 - 1.1_7 \text{ mm.}^{-1} \times t)$ roentgens per hour approximately, if t is not less than 0.3 mm.

Introduction

The practical unit of X-ray quantity has been defined as follows: the roentgen shall be "the quantity of X-radiation which, when the secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in one cubic centimetre of atmospheric air at 0° C. and 76 cm. mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current".

To avoid the wall effect of the chamber it is necessary that its dimensions exceed twice the longest range of the secondary β-rays excited by the X-rays in the air in the chamber. This is impracticable if the radiation is extra hard, for the maximum ranges increase rapidly with the potential applied to the tube from about 13 cm. at 250 kilovolts to a few metres with the highest potentials at present in use. There are a number of possible courses that might be taken to overcome this difficulty. The present unit might be abandoned and another might be chosen that is more convenient for

very hard radiation. The unit might be changed in such a way that it is convenient for very hard radiation, but is approximately equivalent to the present unit in the measurement of soft and medium quality radiation. The unit might be retained, and practical methods of measurement might be devised that would give numerical values that differ by a negligible amount from the results that would be obtained, under certain specified conditions, by applying the present definition literally.

Many physicists who have been associated with medical radiology would regard any change in the definition at the present time as a last resort. There has been a tendency to adopt the third course of devising practical methods that are equivalent, and this has led to the use of small thimble chambers with walls that are described as air equivalent. It is supposed that the ionization per unit volume of air, enclosed by air equivalent walls, is one e.s.u. of charge per roentgen as measured at saturation current at standard temperature and pressure, after allowance has been made for the absorption of the X-rays in penetrating the walls. It is difficult to obtain this condition of air equivalence accurately in chambers constructed of ordinary convenient materials, and the ionization will differ generally by a few per cent from one e.s.u. per cc. per roentgen. However, the method is practicable if this small difference can be determined and added as a correction to the measurement. This can be done with sufficient accuracy for most purposes, by methods that will be described, if the composition of the chamber walls and the approximate quality of the radiation are known.

The density of the ionization in small chambers was first discussed by W. H. Bragg (3) in 1910, and his conclusions were reconsidered by L. H. Gray (6) in the light of the present knowledge of the properties of the rays. Gray has shown that thick walls composed of the light elements are approximately air equivalent if the radiation is sufficiently hard that there is negligible photoelectric absorption of the X-rays in the walls. The correction for the wall effect is obtained by replacing the approximations in Gray's discussion by more precise formulas.

Intensity of Ionization in Thimble Chambers

The theory and calculations in this paper are applicable when the following conditions are satisfied. The chamber is of the same material on all sides except for the insulating bushing where the collecting electrode enters. This bushing is so small that the difference in its composition from the rest of the walls can be disregarded. The collecting electrode is a fine wire, preferably aluminium, with a surface area that is negligibly small compared to the area of the walls. The radiation is so hard that the excitation of photoelectrons, by the X-rays, in the chamber and walls is negligible. The absorption and scattering of the X-rays in the walls is small, and correction can be made for the decrease in intensity due to this cause (see below). The thickness of the walls exceeds the ranges of the secondary β-rays in the wall material and, hence, excludes all secondary β-rays originating outside the chamber.

The following simplifying assumptions are made in deriving the formulas. The air space is so small that the first order excitation of β-rays in it may be neglected, and the change in velocity of β-rays in crossing the chamber can be ignored. This is justified by the experimental finding that the ionization per unit volume in small chambers is independent of the volume of the air space (5)*. The rays are uniform in intensity throughout the walls and inclosed space, and secondary X-rays arising in the walls and the air space are disregarded. Corrections for error arising from this assumption can be made in practice and are discussed later.

If the probability of converting an electron of the wall material into a β-ray of initial energy between $k_o mc^2$ and $(k_o + dk_o)mc^2$, and velocity in the direction given by the polar co-ordinates θ and ϕ by one quantum per square centimetre of X-rays having the direction $\theta = 0$ is $f(\theta) \sin \theta \, d\theta d\phi dk_o$, then it follows that N, the number of β-rays produced in the material per quantum per square centimetre of X-rays, can be expressed by the relation:

$$dN = \frac{\rho_w Z_w}{M_w} f(\theta) \sin \theta \, d\theta d\phi . dx dy dz . dk_o , \qquad (1)$$

in which ρ, Z, and M are respectively density, atomic number, and mass of a single atom, and the subscript w refers to the wall material. The function $f(\theta)$ depends on θ and k_o, but is independent of the other magnitudes.

If the dN β-particles were to continue in a straight path without deflection they would produce in the air space a number of ions, I, given by

$$dI = dN . F(r_w - x) . t \qquad (2)$$

in which x is the distance, in the wall material, from the volume $dx dy dz$ in which the rays originate to the edge of the air space, and t is the length of the path of the particle across the air space, and r_w is the range of the β-rays of energy k_o in the material of which the wall is constructed. The function F will be replaced later by the substitution $F = G(k)$ in which it is expressed as a function of the kinetic energy, T, $(k = T/mc^2)$ of the particle as it enters the space.
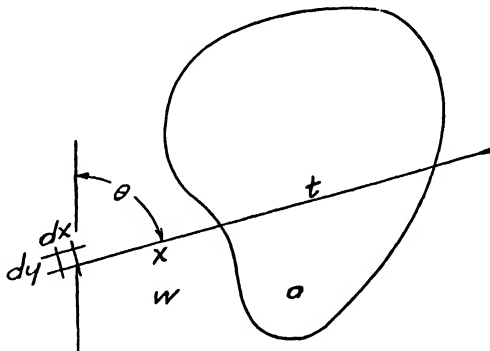
Integration of Equation (2) gives the total number of ions, I, (per quantum per square centimetre) in the air space

$$I = \frac{\rho_w Z_w}{M_w} \int \int \int f(\theta) \sin \theta \, d\theta d\phi \int \int \int_{r_w}^{o} F(r_w - x) t \, dx dy dz \, dk_o . \qquad (3)$$

* *This was also found in unpublished measurements by P. Lowe in this laboratory.*

If, however, a fraction $g\,dp\,d\omega$ of the particles are deflected without appreciable loss of energy (nuclear collisions*), after traveling a distance p, in directions confined by the cone $d\omega$ making an angle ψ with the original direction, the inner triple integral of Equation (3) must be increased by the addition of the terms

$$- g\,dp\,d\omega \iiint_{r_w}^{p} F(r_w - x)\,t\,dx\,dy\,dz + g\,dp\,d\omega \iiint_{r}^{r} F(r_w - q)\,s\cos\psi\,dq\,dy\,dz ,$$
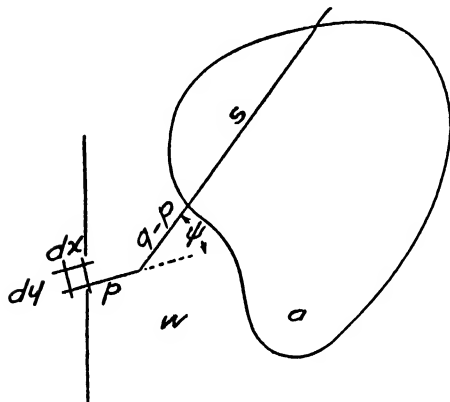
in which q is the total distance traveled by the β-ray to the edge of the space, and s is the distance across the space in this direction. Both of these integrals are equal to

$$V\int_{r_w}^{p} F(r_w - x)\,dx ,$$

where $\iint t\,dy\,dz = V = \iint s\cos\psi\,dy\,dz$ is the volume of the air space. Hence, the two additional terms cancel each other and the total ionization is unaffected by nuclear scattering and is expressed by Equation (3).

This is true, of course, only if all the chamber wall is of the same material throughout. Workmann (15), for example, has found a change in ionization due to reflection in chambers with ends and sides of *different* materials.

The inner triple integral of Equation (3) reduces to

$$V\int_{r_w}^{o} F(r_w - x)\,dx = V\int_{k_o}^{o} G(k) \Big/ \frac{dk}{dx}\,dk .$$

Setting $\mu_w = \iint f(\theta)\sin\theta\,d\theta\,d\phi$, and $\lambda_w = -\dfrac{M_w}{\rho_w Z_w}\dfrac{dk}{dx}$ and substituting in Equation (3) we obtain

$$I = V\int \mu_w \int_0^{k_o} G(k)/\lambda_w\,dk\,dk_o . \tag{4}$$

The intensity of the radiation in roentgens per second is equal to the rate of ionization per unit volume in the imaginary chamber, the "walls" of which are air at standard temperature and pressure. Hence the correction factor for the wall effects is

$$B = \int \mu \int \frac{G}{\lambda_w}\,dk\,dk_o \Big/ \int \mu \int \frac{G}{\lambda_a}\,dk\,dk_o , \tag{5}$$

in which the subscript a refers to air. The subscript is dropped from μ_w and μ_a since they are equal in the absence of photoelectric excitation of β-rays. It will be more convenient to expand this equation in the rapidly converging series

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* *Nuclear collisions, of course, are frequently accompanied by losses of energy due to excitation or ionization that are taken into account in calculating F.*

$$B = 1 + \frac{\int \mu \int \frac{G}{\lambda_a} \frac{\lambda_a - \lambda_w}{\lambda_a} dk\, dk_o}{\int \mu \int \frac{G}{\lambda_a} dk\, dk_o} + \frac{\int \mu \int \frac{G}{\lambda_a} \left(\frac{\lambda_a - \lambda_w}{\lambda_a}\right)^2 dk\, dk_o}{\int \mu \int \frac{G}{\lambda_a} dk\, dk_o} + \cdots \cdots \quad (6)$$

The last term given in Equation (6) may be neglected in most cases.

The ratio G/λ_a is the reciprocal of the average loss of energy of the β-ray per ion formed, expressed in mc^2 units. It is commonly regarded as being quite accurately constant except possibly in the region below $k = 0.05$, which is insignificant in the range of integration of Equation (6). This is expected on theoretical grounds (1, 14), and is supported by experiment to within the accuracy of the difficult measurement of this quantity. These measurements are discussed by Gray (6). Owing to the relative magnitudes of the terms in Equation (6) and the form of the integrands, a 1% variation in G/λ_a, over almost the entire range of integration, would produce 0.05% error in B if G/λ_a is treated as a constant. Therefore, it is justifiable to cancel it as a constant in the numerators and denominators of the second and later terms of Equation (6).

According to Bloch's (2) theory of the rate of loss of energy of the β-rays

$$\lambda = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \left[\log_e \frac{mc^2 \beta^2 W}{1 - \beta^2} - \log P^2 Z^2 + (1 - \beta^2) + R(o) - R\left(\frac{iz}{137\beta}\right) \right]. \quad (7)$$

The symbols e, m, c, β, and z have the usual significance of electronic charge, electronic mass, velocity of light, ratio of velocities of particle and light, and the atomic number of the particle. The maximum energy that it is possible to impart to the orbital electron is represented by W, and is equal to half the kinetic energy of the β-ray. The function $R(x)$ is the real part of $\frac{d}{dx} \log_e \Gamma(x+1)$. The last two terms are negligible for β-rays when $z \ll 137\beta$.

The effective ionization potential, P, is given by $\log_e P = \frac{1}{Z} \Sigma a_n \log P_n$, in which P_n is the ionization potential of the nth electron shell and a_n is the corresponding oscillator strength. It is deduced, from the experimental values of λ for α-rays in penetrating gold, that $\log_e P^2 = 5.205$ (α-ray absorption is used because it is more accurate than similar β-ray data). The introduction of numerical values in Equation (7) gives

$$\lambda = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \left[21.077 + \log \left(k^2 + \frac{k}{2} \right) - \log Z^2 + \frac{1}{(1+k)^2} \right] \quad (8)$$

in which $k = T/mc^2$, and hence,

$$\lambda_a - \lambda_w = \frac{2\pi e^4 z^2}{m^2 c^4} \cdot \frac{1}{\beta^2} \cdot 2 \log Z_w/Z_a . \quad (9)$$

The rate of loss of energy of the β-ray λmc^2 expressed in ergs per centimetre per electron per cubic centimetre of the material has been calculated by several writers. Bloch's (2) theory which is used here is in excellent agree-

ment with experimental data, as may be seen from Tables I and II, in which $s = \lambda \div 2\pi e^4 z^2 / m^2 c^4 \beta^2$ is the quantity in the brackets of Equation (8). Bethe's (1) theory, which appeared just previously, would seem to be more satisfactory in some theoretical respects, but does not agree as well with measurement over a wide range of velocities. For example, Bethe's theory gives a value 30% too low for β-rays in mica at $\beta = 0.96$, and 100% too high for α-rays in very heavy elements. The experimental values of s are deduced from measurements by Gurney, Marsden and Richardson, and Marsden and Taylor (11, p. 140) for α-rays, and from measurements by White and Millington for β-rays (13).

Williams (14) has pointed out that White and Millington's method of determining s excludes the effects of rays that have undergone large energy losses in single collisions. He has shown that this is equivalent to setting W in Equation (7) equal to the constant value of 1500 electron volts. (The exact value is not critical in evaluating s, since it is a factor in a large number of which the logarithm is taken.) This has been taken into account in the calculated values of s for β-rays in Table II. It was considered desirable to publish this table, because in a similar comparison of theory and experiment that was recently published it was apparently overlooked that White and Millington's values exclude the effects of the large individual energy losses.

TABLE I

VALUES OF s FOR α-RAYS OF VELOCITY
1.826 × 10⁹ CM. PER SEC. ($k = 6.6$)
IN DIFFERENT MATERIALS

Substance	s, experimental	s, calculated
H	11.5	11.69
He	9.3	10.31
(Air)	7.64	7.74
Ne	6.7	7.08
Al	6.2	6.56
A	5.9₅	5.91
Cu	5.0₃	4.96
Kr	4.5₈	4.52
Ag	3.7₆	3.99
Xe	4.02	3.71
Au	2.95	2.95

TABLE II

VALUES OF s FOR β-RAYS OF DIFFERENT VELOCITIES IN
MICA MEASURED AND CALCULATED FOR $W = 1500$ E.V.

$\beta = \dfrac{v}{c}$	k	s, experimental	s, calculated
0.64	3.0	10.6	10.6
0.70	4.0	10.7	11.0
0.75	5.3	11.7	11.2
0.80	6.7	12.0	11.5
0.87	10.6	13.4	11.9
0.94	19.6	12.8	12.7
0.96	25.8	13.6	13.1

Substitution of Equations (8) and (9) in Equation (6) and cancellation of $\dfrac{G}{\lambda_a}$ as discussed previously, gives

$$B = 1 + 2 \log Z_w/Z_a \cdot \frac{J}{L} + (2 \log Z_w/Z_a)^2 \frac{K}{L} + \cdots , \qquad (10)$$

with

$$\left. J_\epsilon = \int \mu \int_o^{k_o} \frac{1}{s} \, dk \, dk_o , \quad K_\epsilon = \int \mu \int_o^{k_o} \frac{1}{s^2} \, dk \, dk_o , \quad L_\epsilon = \int \mu k_o dk_o \right\} \quad (11)$$

and $\quad s = 21.077 + \log (k^2 + k/2) - 3.948 + 1/(1 + k)^2$

in which the s throughout refers to air.

For monochromatic rays of energy $h\nu = \epsilon mc^2$, $K = K_\epsilon$, $L = L_\epsilon$, and $J = J_\epsilon$. For a continuous spectrum having dQ quanta in the range of quality $d\epsilon$,

$$J = \int \frac{dQ}{d\epsilon} J_\epsilon d\epsilon, \qquad K = \int \frac{dQ}{d\epsilon} K_\epsilon d\epsilon, \text{ and } \quad L = \int \frac{dQ}{d\epsilon} L_\epsilon d\epsilon . \qquad (12)$$

The integrals $\int_o^{k_o} \frac{dk}{s}$ and $\int_o^{k_o} \frac{dk}{s^2}$ are plotted as functions of $k_o = T/mc^2$ in Fig. 1.

The values of s for very small values of k were taken directly from experimental data of electron absorption coefficients, because the theory is not valid at very low energies. The integration was performed graphically.
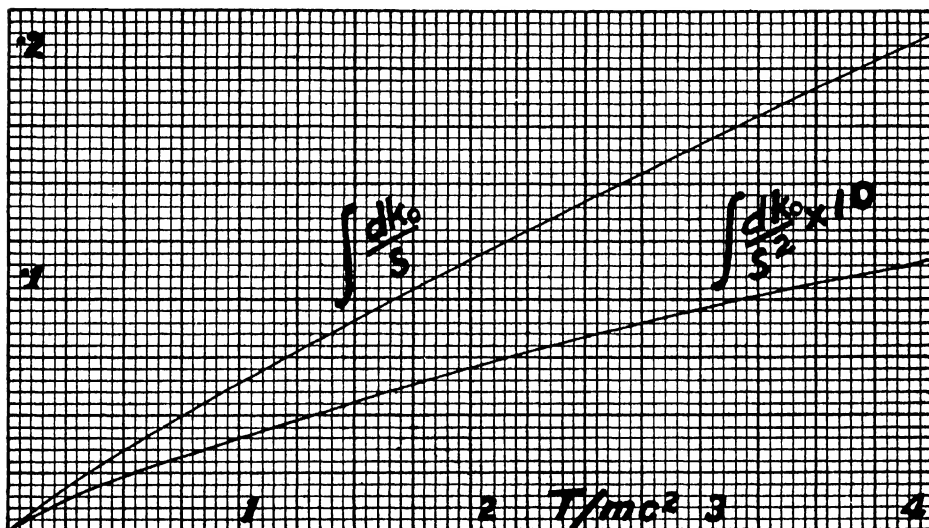
FIG. 1.

Some values of $2 \log Z_w/Z_a$ and $(2 \log Z_w/Z_a)^2$ are given in Table III. When the wall material is composed of more than one element, $2 \log Z_w/Z_a$ is replaced by $(\Sigma 2 n_z Z \log Z/Z_a)/\Sigma n_z Z$, in which n_z is the relative number of atoms of the element of atomic number Z.

The number of β-rays, μdk_o, in the energy range dk_o, produced per electron of material by one quantum of X-rays of energy $h\nu = \epsilon mc^2$ per square centimetre is obtained by simple trigonometry from

TABLE III

Material	Z_w	$2 \log Z_w/Z_a$	$(2 \log Z_w/Z_a)^2$
H	1	-3.948	15.59
Li	3	-1.752	3.07
Be	4	-1.176	1.38
B	5	-0.730	0.53
C	6	-0.364	0.13
N	7	-0.052	0.00
O	8	0.226	0.05
F	9	0.446	0.20
Na	11	0.848	0.72
Mg	12	1.022	1.04
Al	13	1.182	1.40
S	16	2.786	7.73
Air	(7.2)	0	0
Water	(5.3)	-0.609	0.37
Bakelite	—	-0.657	0.43
Amber	—	-1.100	1.21
Cellulose	—	-0.506	0.26
Elektron	—	1.088	1 18

Klein and Nishina's (8) theory of modified scattering:

$$\mu = 4.93 \times 10^{-25} \cdot \frac{1}{\epsilon^2}\left(1 - \frac{1}{\epsilon}\frac{\xi}{\zeta} + \frac{1}{2\epsilon^2}\frac{\xi}{\zeta} + \frac{1}{2}\frac{\xi^2}{\zeta}\right),\tag{13}$$

in which $\xi = k_0/h\nu$ and $\zeta = 1 - \xi$. ($\zeta h\nu$ is the energy of the scattered quantum.) The maximum value of $\xi\epsilon$ is $\dfrac{2\epsilon^2}{1 + 2\epsilon}$, and at that energy

$$\mu = 4.93 \times 10^{-25} \cdot \frac{1}{\epsilon}(1 + \xi\epsilon).$$

The values of J_ϵ, K_ϵ and L_ϵ for one quantum of X-rays of energy $h\nu = \epsilon mc^2$ are obtained by substituting Equation (13) in Equation (11). They are plotted in Fig. 2.

Absolute Evaluation of X-ray and γ-Ray Intensities

The formulas may also be applied in the determination of intensities in quanta per square centimetre per second. The ionization current, c, per unit volume of air per second produced by one quantum of radiation of energy $mc^2\epsilon$ per square centimetre per second is, from Equation (4),

$$c = e \int \mu \int_0^{k_0} G(k)/\lambda_w dk \, dk_o .$$

Substitution from Equations (10) and (11) gives

$$c = eBL_\epsilon G(k)/\lambda_a .$$

The ratio $\lambda_a/G(k)$ is the loss in energy in mc^2 units per ion formed per electron in a cubic centimetre of air. Introducing numerical values, and taking the energy loss per ion as 32.5 electron volts,* we have for the current density

$$c = BL_\epsilon \times 2.92 \times 10^{15} \text{ e.s.u. per cc.},\tag{14}$$

when the air in the chamber is at standard temperature and pressure.

Intensity of Radiation from Radium B and C

The thimble chamber method has been used in determining the intensity of the radiation, in roentgens per hour, at unit distance from 1 mg. of radium in equilibrium with its decay products, and enclosed in platinum with an effective wall thickness of 0.5 mm. Besides being an evaluation of an important constant, these measurements are a test of the reliability of thimble chamber measurements as carried out in different laboratories under different conditions. Some of the early measurements disagreed badly, but since the possible sources of error have become better understood most of the recent determinations are in good agreement when correction is made for the wall effect by the methods just described. Some very recent measurements are given in Table IV, with the experimental values reduced where necessary to 0.5 mm. platinum filtration listed in the third column, and the values fully corrected for the wall effect listed in the last column. The average of these

* See Reference (6).
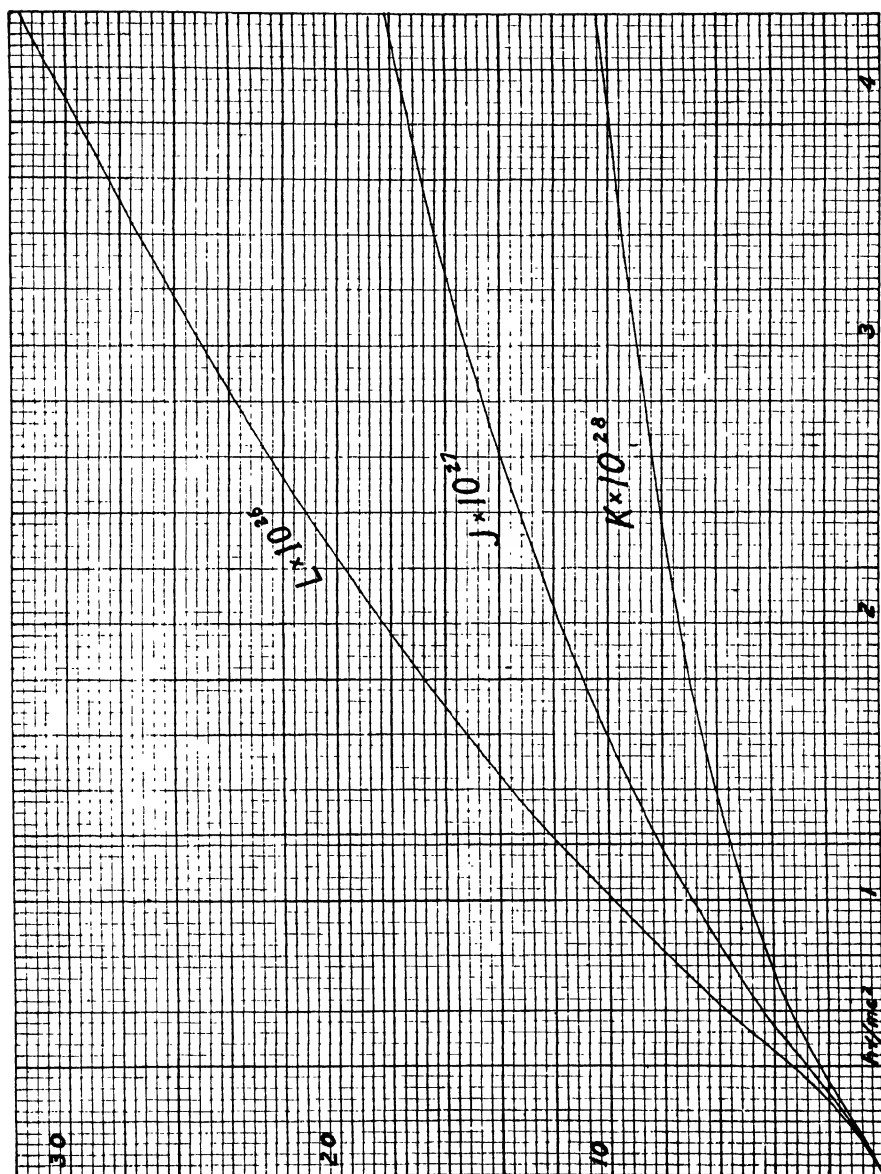
FIG. 2. Values of K_e, J_e and L_e plotted as functions of $\epsilon = \dfrac{h\nu}{mc^2}$.

TABLE IV

Authority	Reference	Measured intensity	Chamber wall	B	Corrected intensity
Friedrich, R. and Schulze, W.	5, p. 567	7.8	Carbon	0.977	8.0
Murdoch, J. and Stahel, E.	10	8.05	Ebonite	0.959	8.4
		8.29	Paper	0.968	8.6
Mayneord, W. V. and Roberts, J. E.	9	8.3	Carbon	0.977	8.5
Sievert, R. M.	12	7.7	Celluloid	0.968	7.9_5
Grimmett, L. G. and Read, J.	7	9.4	Elektron	1.074	8.6_5
			Mean value		8.3_5

is 8.3_5 roentgens per hour, and their mean deviation from the average is about $2\frac{1}{2}\%$. The intensity of the radiation may be expressed in more general terms, to apply to any thickness, t, of platinum wall, as

$$(8.9_8 - 1.1_7 \, mm^{-1} \times t) \, \frac{\text{roentgens}}{\text{hours}} \Big/ \frac{\text{mg.}}{\text{sq. cm.}} \, ,$$

with sufficient accuracy for practical purposes if t is not less than 0.3 mm.

In the calculation of J, K, and L for the γ-rays from this standard radium source, Ellis and Wooster's (4) values of the absolute intensities from radium B and C were used after correction was made for the absorption in 0.5 mm. of platinum. The amount of γ-radiation from radium and radium E and of X-radiation resulting from internal conversion and fluorescence that penetrates the platinum is negligible in these calculations. The secondary or scattered radiation arising in the platinum produces about 5% of the ionization in the chamber. Its spectral distribution was calculated approximately by the Klein and Nishina theory. It is difficult to calculate the absorption of the scattered radiation accurately because it depends on the shape of the container, but the uncertainty in J/L and K/L due to this cause is less than $\frac{1}{2}\%$ and has negligible significance in B.

The values obtained for the total radiation from radium in equilibrium with its decay products and enclosed in platinum with effective wall thickness of 0.5 mm. are $J/L = 0.064_4$, $K/L = 0.003_9$. Typical values of B with this source for different wall materials are: carbon, 0.977; elektron (90% magnesium), 1.074; aluminium, 1.081; bakelite*, 0.959; wood and cellulose products, 0.968; amber*, 0.934.

The comparison by Gray (6) of the ionization densities in chambers constructed of different materials permits a partial check of these calculated corrections. Using radium in equilibrium and filtered by 0.5 mm. of platinum and 2 cm. of lead he found, for example, that the ionization currents in aluminium and carbon chambers of the same internal dimensions were in the ratio 1.098. This agrees satisfactorily with the ratio 1.103 in the calculated values of B for these materials with the same quality of radiation.

*The following approximate compositions in relative numbers of atoms were used in calculating B: bakelite, 43 C + 38 H + 7 O; amber, 50 C + 80 H + 5 O + S.

Measurement of Extra Hard X-rays

A variety of filtrations and other conditions are used with therapeutic high voltage X-ray tubes, and B must be determined for individual cases. Approximate values that are accurate enough for many practical purposes may be estimated by inspection of Fig. 2 without carrying out the integration of Equations (12). For example, when 600 kv. is used with a filtration of 1 mm. lead and secondary filters to absorb the secondary radiation from the lead, the spectrum extends from 0.2 to 1.2 mc^2 units. At the lower limit J/L (from Fig. 2) is 0.09, and at the upper limit, 0.069. The correct value that would be obtained by Equations (12) must be between these and closer to the latter, and a good estimate is 0.07_5. If a carbon chamber is used (see Table III) $B = 1 + (-0.36 \times 0.07_5) + \ldots = 0.97_3$ to within $\frac{1}{2}\%$. In more accurate calculations of B by the use of Equations (12), the spectrum must be described by $dQ/d\epsilon$ expressed as a function of $mc^2\epsilon$. In these terms, the spectrum of the radiation from the anticathode before penetrating the tube walls and filters may be represented on a graph very approximately by an oblique straight line that intercepts the $mc^2\epsilon$ axis at the point corresponding to the maximum frequency in the spectrum. If this curve is corrected for the absorption in penetrating the filters, the resulting curve will describe the spectrum transmitted with sufficient accuracy for determinations of B for ordinary purposes. (It will be seen from the discussion in the previous paragraph that B is not very sensitive to error in the shape of this curve. The difference in the spectrum from constant potential and from rectified sine wave excitation makes negligible change in its value.)

Accuracy and Absorption Corrections

The second and third terms in the expansion of B by Equation (10) are usually only a few per cent of its total value. The expressions that were used in evaluating μ and λ in these terms are probably accurate to within a few per cent, and, therefore, the uncertainty in B due to this cause is less than 0.1%. The accuracy is limited by the simplifying assumptions about absorption, scattering, and uniformity of intensity that were made in deriving Equation (10), or the accuracy with which corrections can be made for these sources of error. Absorption and scattering in the chamber wall are conveniently considered together because their combined effects can be regarded and measured as "apparent absorption". In the almost complete absence of the photoelectric effect the apparent absorption is much smaller (four times smaller in a typical case) than the true absorption, since the absorption of a quantum is accompanied by the emission of the scattered softer quantum in a direction most probably forward.

The obvious method of determining the apparent absorption is by measuring the ionization current with increasing thicknesses of chamber wall effected by adding shells of the same material on the outside of the original wall, which is of the least thickness that is impermeable to the fastest β-rays. Correction for the absorption and scattering in the walls is made then by extrapolation

to zero wall thickness. For this purpose it is very desirable that the wall and shells be of uniform thickness on all sides (and preferable that they are spherical) for the following reason. If the chamber wall is of simple shape and uniform thickness, the relative geometrical distribution of the scattered radiation is altered very little when the wall thickness is increased uniformly, and the change in the intensity of the radiation scattered from the walls is approximately proportional to the wall thickness.

The fact that the intensity of the X-rays is not quite uniform throughout the walls on account of absorption and the inverse square law, violates basic assumptions made in the derivation of the formulas, and thereby introduces a small error in the small second and third terms of B that is negligible in the total value of B for all ordinary conditions. However, the inverse square law causes a displacement of the apparent centre of the chamber towards the radiation source from the geometrical centre of the air space by a distance of the order of $\frac{1}{2}V^{\frac{1}{3}} \div R$, which is appreciable when the distance from the source is very small.

One of the most frequent measurements in radiotherapy is the determination of the skin exposure. Errors in this may be reduced by the practice of placing a slab at least 1 cm. thick of bakelite or other organic material of about the same density as flesh over the exposed skin. If this is done the skin is no longer a free surface exposed to β-rays from the filters, and the variation with depth in the tissue of the intensity of the scattered radiation is decreased. If the ionization chamber is built into this slab, the skin exposure can be obtained by correcting for absorption and inverse square law with less error than is usual in the measurement of skin dosage.

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AUTOMATIC GAIN CONTROL[1]

By E. C. JORDAN[2]

Abstract

The simple, automatic volume control circuit of radio receivers has been adapted for use in the studio amplifier of a broadcasting station to give a semi-automatic control of programs. The circuit adjustments for optimum control action were determined experimentally, and then this control action was analyzed by means of oscillograms. The effects of different time constants and degrees of control were noted, and methods for varying the latter indicated. The circuit is shown to be distortionless, except in so far as manual control of amplifier gain may be said to introduce "distortion". The control action, while not fully automatic, is complete enough to be of real assistance to the operator.

Introduction

The full volume range of music in a broadcast program is some 65 or 75 decibels. The transmission of such a large range is difficult owing to limitations imposed, on one hand, by the minimum level of the inherent noises of the system, and, on the other hand, by the maximum signal level that can be handled without distortion. Moreover, experiments have shown that under average home conditions the range between the loudest comfortable listening level and the lowest volume sufficient to overcome background noise of both the room and the receiver is about 40 decibels. For these reasons it is necessary to "control" a program, and this is one of the chief duties of a control operator. It would seem, however, that this controlling might be done, to some extent, automatically. It was the purpose of this investigation to adapt the automatic volume control circuits of radio receivers to a broadcast audio-amplifier, and then to determine the nature and efficacy of the control action so produced.

Experimental

The principle of the usual automatic volume control circuits is to rectify some of the output of the last radio-frequency stage, filter it and apply the slowly varying d-c. component to the grids of the variable-μ tubes of the previous stages. The circuit shown in Fig. 1 was developed for the audio-frequency amplifier used. The control circuit proper is shown in heavy lines and consists of the transformer Tr_1, potentiometer P_1, tube T_3, and the filter network C and R. Tube T_2 and its associated circuit are for volume indication, and, while not necessary in the functioning of the control, they are helpful in determining the extent of the action. The first tube of the amplifier, a

triode, was replaced by a tetrode, T_1, of the variable-μ type. The rectifier tube, T_3, is normally biassed beyond cut-off; this prevents the flow of plate current through the resistor R, and operates the variable-μ tube T_1 under a condition of minimum bias and, hence, maximum amplification. When a signal voltage is applied to the amplifier it appears at the input of the rectifier, and a plate

FIG. 1. *Studio broadcast-amplifier with automatic gain control circuit.*

current, whose average is proportional to the amplitude of the signal voltage flows through the circuit. This current flowing through R applies an additional bias to tube T_1. The reduction in gain is proportional to the amplitude of the signal voltage, and is slight for low volumes and comparatively great for high volumes. There is thus accomplished a simple form of automatic control.

Discussion

The nature of this control action can best be understood by a study of the oscillograms (Figs. 2, 3, 4, and 5 (Plates I and II)). Fig. 2 shows a series of eight still pictures of the amplifier output voltage when the input was a pure 300 cycle note. The pictures show conditions at approximately 1/40 sec. intervals over a period during which the input level was increased eight decibels. The first picture of Fig. 2, *a*, shows the initial output. The second shows the increased output immediately after the input level had been raised. The remainder show the action of the control in reducing the amplitude to the final level of the second last picture in Fig. 2, *c*. The last picture shows, for comparison, the increased output level that would have been obtained without any control action. The oscillograms of Fig. 3 give a continuous record of the amplifier output over a period of about one second, during which time the 300 cycle input voltage was increased ten decibels for about 3/10 sec. and then decreased again. (The ticks indicate tenths of seconds.) Fig. 3, *a*, shows the output uncontrolled. Fig. 3, *b*, *c* and *d*, show the output with the automatic control in operation. In *b* the control operates to reduce the gain on the louder signal, while in *c* and *d* (*c* and *d* are continuations of *b*),

PLATE I

FIG. 2

FIG. 3

FIG. 2. *A series of pictures of a 300 cycle note, the volume of which is being reduced by the control.* FIG. 3. *A 300 cycle note during a sharp increase and decrease in volume. (a) Without the control; (b, c and d) with the automatic control, (e and f) with the control and using very short time constants.*

the gain is being slowly increased by the control after the input level was decreased. Note that although it takes only about 1/5 sec. to reduce the gain on a peak it requires nearly a full second to return the gain to normal after the peak has passed. This is necessary to preserve the naturalness of reproduction. In Fig. 3, *e* and *f* are similar to *b*, *c*, and *d*, except that shorter time constants were used. Figs. 4 and 5 are oscillograms of a soprano and baritone voice, respectively, during peak passages in a song; *a* and *b* in each case show the passages uncontrolled, while *c* and *d* show the same passages automatically controlled. The timing wave of Fig. 4 is 60 cycles, while the ticks of Fig. 5 indicate 1/5 sec. These oscillograms indicate the manner in
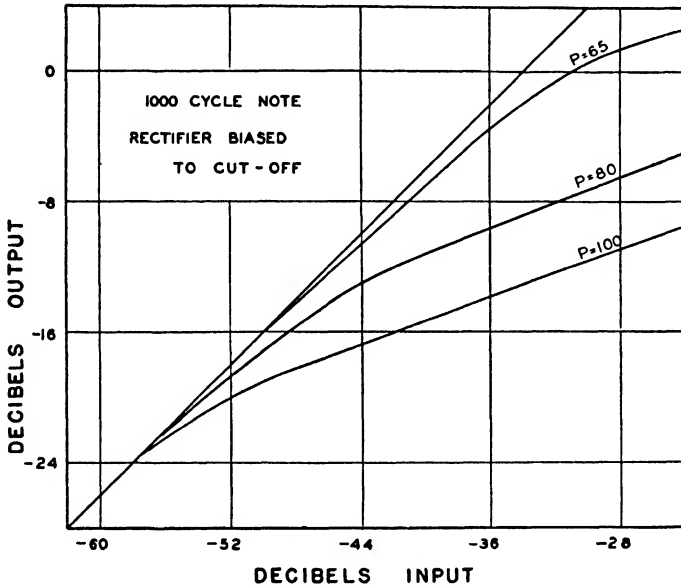
FIG. 6. *Amplifier input-output curves for different degrees of automatic control action.*

which the gain changes with variations in input level. The quantitative relation between gain and input level is given by the input-output curves of Fig. 6.

From the curves of Fig. 6 it can be seen that for all input levels up to about −60 db. the amplifier gain is constant at 34 db., but that for input levels higher than −60 db. (depending on the setting of P_1) the gain is reduced by an amount that depends on the average volume level of the signal. Over a small interval of time, however, this reduction in gain is the same for all components of the signal voltage, regardless of frequency or amplitude. The slope of the curve indicates the contraction that will occur in the output volume range. In practice if the slope is not great enough, that is, if the contraction is too large, the output will be of almost a constant level and the music will lack "depth" and "contrast"; on the other hand, too great a slope, approaching unity, will give insufficient control action. The setting of P_1 determines the strength of the control action for a given output voltage, and

so for a fixed rectifier bias determines the output voltage at which the control becomes effective. It will be seen from Fig. 6 that the slope of the upper portion of all the curves is almost the same, and, therefore, independent of P_1. For an amplifier with a variable-μ tube, the following relation holds fairly approximately over the operating range of the tube—

$$E_0 = \frac{K}{V^a} E_i ,$$

where E_0 = output signal voltage, E_i = input signal voltage, V = grid bias on the tube, K is a constant, and a is a parameter of the variable-μ tube. From this relation it can be shown that the slope of the input-output decibel curve is given by

$$\text{Slope} = \frac{1}{pa + 1}$$

where p is constant for the rectifier used ($p = 1$ for linear rectification, and $p = 2$ for square law rectification). Because a is determined by the choice of variable-μ tube, the only other means of changing the slope of the input-output curve is through the type of rectification used. Curve 2 of Fig. 7
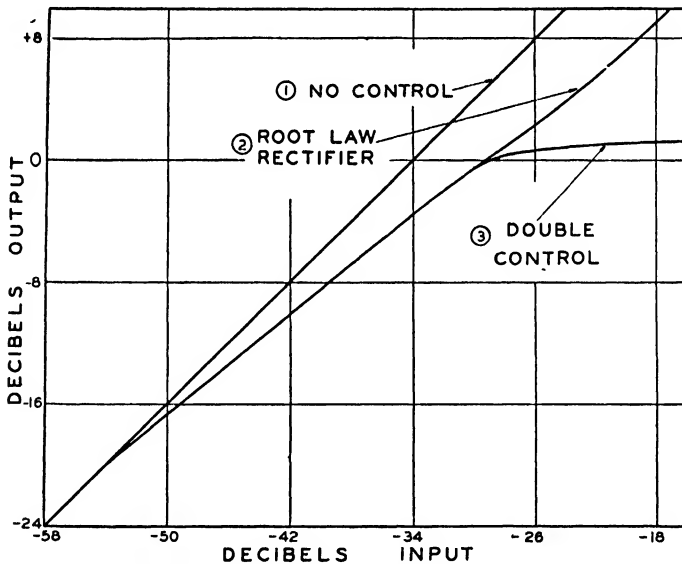
FIG. 7. *Amplifier input-output curves. 1. Without automatic control. 2. With the control of Fig. 1 using a root-law rectifier. 3. With the control of Fig. 8.*

shows an increased slope obtained by the use of a rectifier whose output varied approximately as the square root of the input voltage. This curve is very nearly straight over a 34 db. range. A control action that possesses the cut-off characteristic shown by Curve 3 is effective in limiting the amplifier output to a predetermined maximum (say, corresponding to 100% modulation) and so gives a "safety valve" action as well as the gradual control over the normal range. It may be obtained with the circuit of Fig. 8 in which a

high gain tube is connected in parallel with the usual rectifier but arranged with a larger bias, so that it does not become operative until the desired output voltage is reached. Fortunately, however, the simple circuit of Fig. 1 gives a control action quite satisfactory in practice.
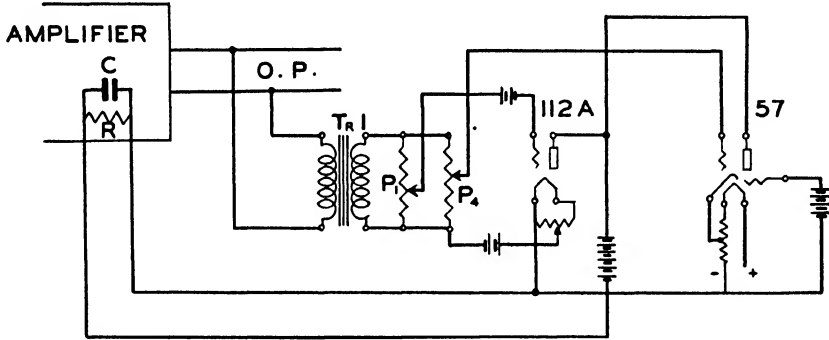
FIG. 8. *A control circuit giving an added "safety-valve" action.*

The smooth operation of the control depends largely upon the selection of suitable time constants. These are the times to (i) reduce or (ii) increase the gain when the input level changes. The first is the time required to charge the condenser C through the plate resistance of the rectifier (although the shunt resistance R decreases this slightly), while the second is the time required to discharge the condenser through R. Too long a time for (i) makes the control sluggish and slow, while a very short time gives too sharp a reduction, and produces, on high peaks, a throttling or choking effect similar to that observed when the manual control is operated too quickly. This time should be longer than one-quarter of the period of the lowest note it is desired to amplify. The time required to raise the gain on a soft passage after a louder passage has passed is important. If too short a time is used, say 1/10 sec., the control increases the volume too rapidly on a soft passage and some of the artistic effect is destroyed. If a very long time-constant, such as five seconds, is used, then, when the gain is decreased by a high peak it remains at this reduced level for so long a period that, if these peaks occur at all frequently, the average level of the program will be maintained too low. The optimum value for this latter time however is not too critical and was selected as 0.8 sec., although any time within the range of $\frac{1}{2}$ to 2 sec. is fairly satisfactory.

For such a control to be acceptable as part of a broadcast amplifier it is essential that the amplification remain distortionless. At those times when the input signal level to the amplifier is relatively steady, the control bias on T_1 is constant, and the amplifier operation, as far as phase, amplitude, and frequency distortion are concerned, is identical with the uncontrolled operation except for the increased bias on tube T_1. The primary winding of the interstage transformer Tr_2 is shunted by a resistor R_2 of a value approximately equal to the plate resistance of the replaced triode, so that the frequency response of this stage remains unchanged. The filter circuit C, R, C_1, R_1,

between input and output effectively prevents regeneration or degeneration effects. However, during those periods when the amplifier gain is changing from one level to another the question of transitory distortion arises. To investigate conditions during these transition periods the oscillograms were taken. Those of Fig. 2 show the wave form of a 300 cycle note immediately before and during a transition period. The only discernible difference is the gradual decrease in amplitude, the trace retaining its pure sine wave shape. The continuous film oscillograms of Figs. 3, 4, and 5 show how the wave envelope expands and contracts with the changing bias without affecting the shape of the individual waves. From Fig. 3, *a* and *b*, is obtained a comparison of manual and automatic control. Fig. 3, *a*, shows the result of a rather rapid manual operation. The increase and decrease in amplitude take place in small but discontinuous steps. With automatic control (Fig. 3, *b*, *c*, and *d*) the amplitude decreases and increases gradually according to an exponential law Ae^{-x}, and the action is seen to be much less abrupt and therefore less noticeable than that of the manual control. The automatic volume reductions shown in Figs. 4 and 5 occurred on very sudden high peaks, and are more rapid than is usually the case, but they were taken to show the control under the most severe conditions. The changes in gain occurring normally are so gradual as to be imperceptible in an oscillogram covering only one or two seconds.

The operating technique with the control functioning is simple. As before, the manual attenuator control is opened at the beginning of each selection, and, with the aid of the volume indicator, Ma_2, and control action indicator, Ma_1, is set at approximately the correct position for the particular selection. The automatic control then keeps the volume range within the desired limits. Should the operator err in his judgment and set his gain too high, there is no unpleasant blasting as would result ordinarily—he merely observes on meter Ma_1 that the control action is stronger than normal and reduces it at his leisure.

Conclusions

The curves of Fig. 6 indicate that the control action of the simple circuit of Fig. 1 is not fully automatic. The volume contractions occur only on the upper 30 db. of the complete 60 or 70 db. range. A completely automatic control, *i.e.*, one that would contract uniformly a 70 db. range to 30 or 40 db., might be obtained with a more complicated circuit, but such action is not desirable. It would necessitate reductions in volume too great to pass unnoticed, and the in-between-selection noises (artist's movements, rustle of pages, etc.) being transmitted at maximum gain would prove objectionable unless reduced manually. The presence of an operator is essential, but the semi-automatic gain control will perform for him the continual controlling throughout the selection.

Acknowledgment

THE RADIAL-STEREOPLOTTER[1]

BY E. L. M. BURNS[2] AND R. H. FIELD[3]

Abstract

A machine for plotting from air photographs, by the radial line method, has been developed by the Associate Research Committee on Surveys. The purpose of the plotter is to increase the accuracy and speed of extending minor control through strips of photographs by this method which is so widely used in Canada.

A description of the machine is given, preceded by a brief explanation of the principles underlying its design.

The methods so far employed in using the plotter are explained together with an examination of the sources of error arising in these methods, some of which are of general application to radial line plotting. Owing to the short time that the radial-stereoplotter has been in operation, conclusive statements cannot be made as to the results it will give when handled by an experienced operator, but already there is evidence of a considerable saving of time and gain in accuracy as compared with hand graphical methods of extending radial line control.

Introduction

The Subcommittee on Mapping Methods of the Associate Research Committee on Surveys, in its efforts to develop those forms of air photogrammetry peculiarly applicable to Canadian conditions, *i.e.*, the need for small-scale maps produced as cheaply and efficiently as possible, has sponsored the construction of a machine for extending control by radial intersection through strips of air photographs. The principles of the plotter were developed by Colonel Burns, and the design and construction of the first model was undertaken by the staff of the National Research Council in co-operation with him.

Radial Intersection Control

The radial line method of extending control is now well established. It is discussed in References (1) and (2), and depends on the fact that for the case of vertical air photographs the distortion due to elevation differences and to small tilts may be regarded as radial from the principal point (2, p. 69). This permits nets of triangles to be extended through a strip of overlapping photographs, the corners of the triangles being formed by the ground plans (plotted to a uniform scale) of the principal points of consecutive photographs and of convenient details near the margins (minor control points). The points so plotted form a system of control for the transfer of detail from the photographs to the map.

Fundamental Considerations

Let Fig. 1 represent two consecutive vertical (untilted) photographs placed so that the principal point of the right-hand photograph, P_1, is placed over the image of the corresponding detail in the left-hand photograph, and one

of the photographs is rotated about this point until the image of the detail corresponding to P, the principal point of the left-hand photograph, falls on the line PP_1; PP_1 is the projection of the air base, or line joining the two positions of the camera lens at the respective instants of exposure.   Let A represent the image of a detail on the ground as registered on the left-hand photograph, and A_1 represent the image of the same detail on the right-hand photograph.   If the photographs were untilted, undistorted, taken at the same altitude and the elevations of the three points P, P_1, and A were the same, A and A_1 would coincide.   If this does not occur, and the tilt is small, the point a where AP and A_1P_1 intersect is the ground plan, to the scale set by the length of PP_1, of the detail represented by A with respect to PP_1.   Perspective considerations show that A_1A is parallel to PP_1, for it is the trace on the photographs of a plane passing through the lens and parallel to PP_1.   Relative tilt in the photographs will cause a departure from this parallelism.
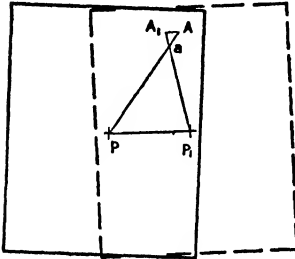
<div align="center">FIG. 1.</div>

With the photographs placed as in Fig. 1, a linkage could be imagined consisting of two rods, pivoted respectively at P and P_1, which would serve to determine the true shape of triangles formed by the ground plans of the points P, P_1, and A.   To make such a scheme feasible it would be necessary to separate the photographs so that both were visible at once, and conditions would become as indicated in Fig. 2.   The right-hand photograph is moved
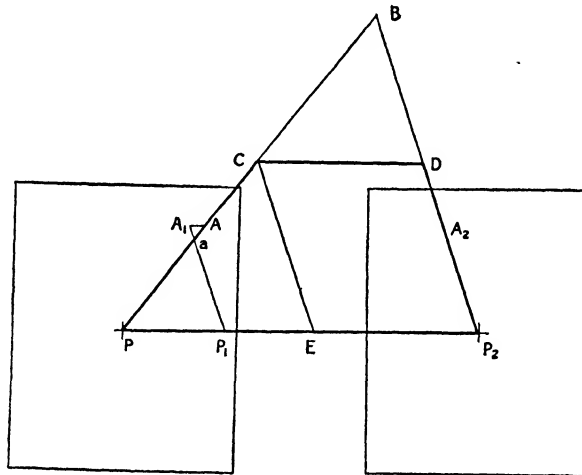
<div align="center">FIG. 2.</div>

by an amount P_1P_2, and A_1 moves to A_2.   Produce PA and P_2A_2 to intersect at B.   The triangle BPP_2 is similar to the triangle aPP_1.   This is quite general, and as the two radial arms PA and P_2A_2 were directed over the corresponding images of ground detail, the various positions of B would,

if plotted, form a figure similar to that traced by the various positions of a, with the photographs superimposed as in Fig. 1. The scale of the plot of B's positions is obviously $\dfrac{PP_2}{PP_1}$ times the scale of the plot of a's positions. It follows, with the method visualized, that the scale can be adjusted by altering the length PP_2, but it is impracticable to reduce the scale to the extent that the photographs touch each other.

The scale may be reduced still further by the following modification. Draw CD parallel to PP_2, intersecting the radial lines in C and D. Draw CE parallel to P_2A_2, intersecting PP_2 in E. If CD remains parallel to PP_2 and of a constant length, as B moves from point to point, the triangle CPE will always be similar to BPP_2, and therefore C will trace a similar figure to B, but at a scale $\dfrac{PE}{PP_1}$ of the scale of the figure traced by a. In this way, by choosing the fixed length of CD we can arrange so that any convenient point in it (to which a pencil could be attached) would plot the plan positions of the detail registered on the overlapping photographs to a scale such that the air base was represented by the length $(PP_2 - CD)$.

In the radial-stereoplotter it is not practicable to use all parts of the figure CDP_2P in one plane, but the arms PA and P_2A_2, which determine the angles APP_1 and A_1P_1P, are in one plane, and in another, the arms CP and DP_2 move respectively parallel to them. The link or bridge CD is adjustable to determine the plotting scale, *i.e.*, by making the lines joining the plotted positions of selected points coincide with the lengths already plotted from the previous pair of photographs. The scale is chosen by setting the length of CD equal to a convenient amount when the first pair of a strip is plotted.

This device may be considered as an adaptation of the well known Zeiss parallelogram, so named about the time it was first used by Pulfrich and his assistants in the Zeiss Stereo-autograph for plotting terrestrial photographs. A further discussion of its properties will be found in References (2) and (5).

Principle of the Radial-stereoplotter

Imagine two consecutive photographs (a stereoscopic pair) oriented so that the air base lies along PP_1, Fig. 3, *i.e.*, set in the same relative orientation as at the respective instants of exposure, all tilts being ignored. In the plotter, the photographs are clipped on tables and have the principal points set over the centres of rotation, so that this adjustment is easily made (2, p. 34). A magnifying stereoscope D is provided with mirrors M and M_1, and by means of a right- and left-handed screw the distance MM_1 can be altered until it is possible to set the stereoscope so that the images, A and A_1, of a given detail are focused respectively on the reticules of the left- and right-hand telescopes of the stereoscope. The reticule marks (floating mark) of the stereoscope will then appear to lie on the ground at the point in question (2, p. 26) according to the well known principles of stereoscopy.
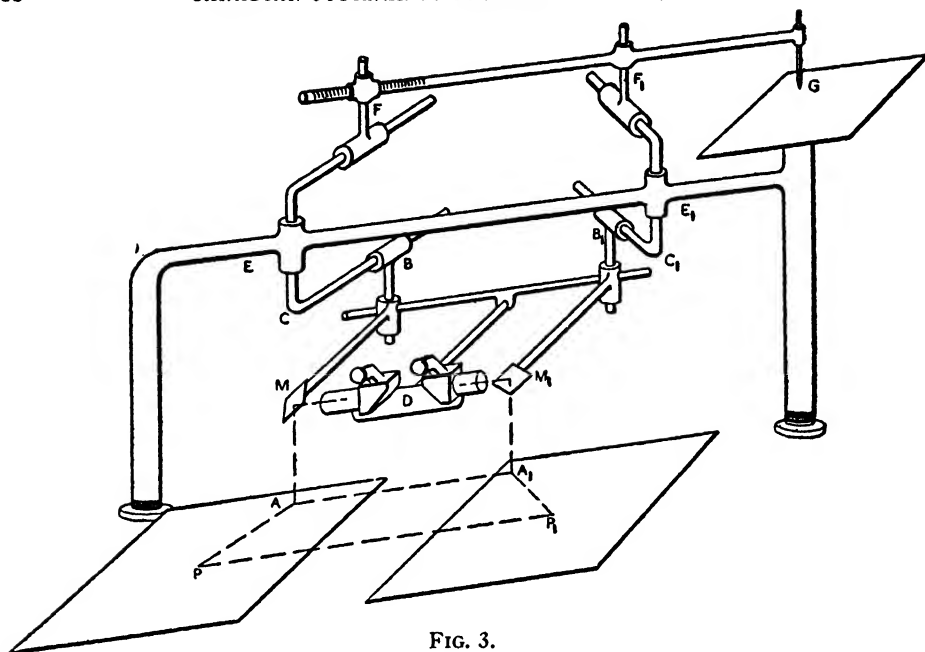
FIG. 3.

The brackets carrying the mirrors bear pivots at B and B_1, the upper parts of these pivots being fitted with slides on which engage arms CB and C_1B_1, which are free to swing about fixed pivots at E and E_1. The mirrors are adjusted until B is under E, when the left telescope is directed on P, and similarly for the right telescope. The horizontal projections of EE_1 and PP_1 then form a rectangle, and it is readily seen that the horizontal projection of EBB_1E_1 is similar and equal to that of PAA_1P_1, *i.e.*, we have the figure PAA_2P_2 in Fig. 2.

For plotting purposes two additional radial arms, above the pivots E and E_1, move parallel to the lower arms. A bridge FF_1G, constrained so as always to remain parallel to EE_1, is fitted with pivoted slides at F and F_1 in which the upper radial arms engage, thus forming a "Zeiss parallelogram". Any point on FF_1G, say G, will plot the relative plan positions of the points properly sighted on by the stereoscope to a scale at which the length, $(EE_1 - FF_1)$, represents the horizontal projected length of the air base PP_1. This scale may be quite different from that of the photographs.

PLATE I

FIG. 4. *The radial-stereoplotter.* FIG. 5. *The plotter without the upper and lower carriages. The upper radial arms, their fixed pivot bearings, and the plotting table are visible, as well as the handwheel and most of the mechanism for moving the lower carriage slowly in the Y direction.* FIG. 6. *The lower carriage, showing the mechanism for moving the stereoscope along the carriage in the X direction. The stereo telescopes and the mirror brackets, with the pivots which engage with the lower radial arms, are seen, as well as the two tubes along which the mirror brackets slide when parallax (Z direction) adjustments are made.* FIG. 7. *The upper carriage. The X and Y direction guide bars are clearly seen, as well as the triangular plates on the end of the pivots which engage with the upper radial arms. The spacing of these pivots determines the plotting scale. The plotting pencil is carried from the tube seen extending to the right.*

PLATE I
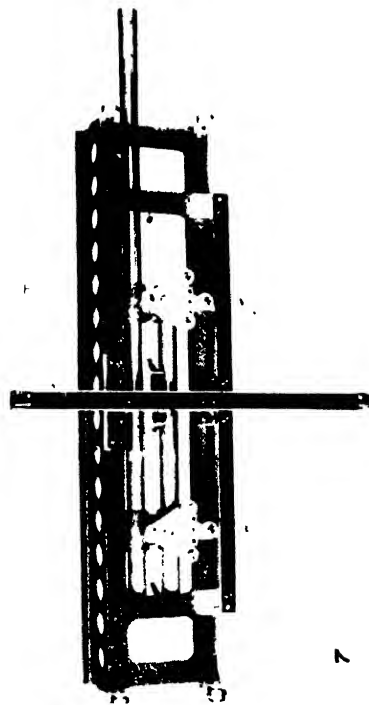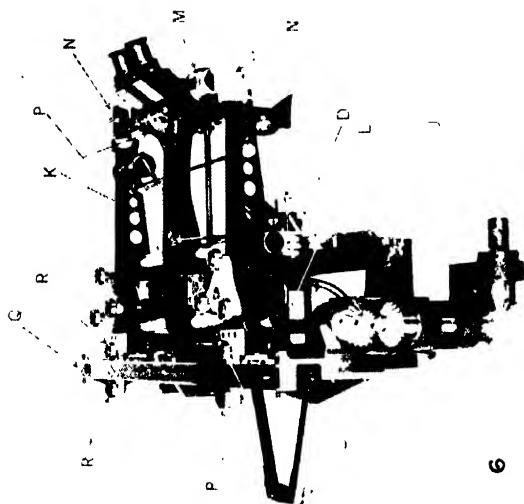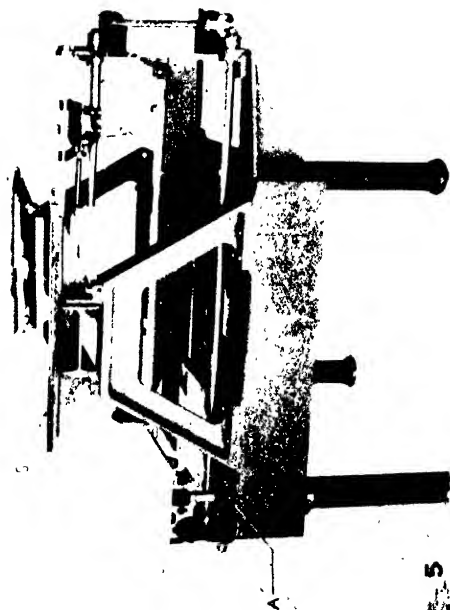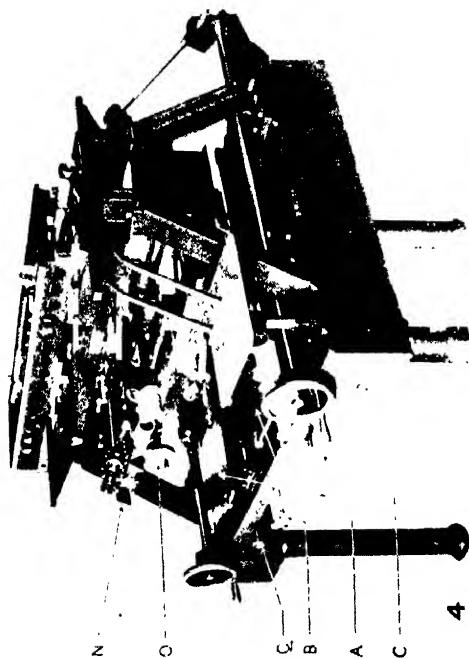
It should be observed that the radial intersection method of plotting fails when the two rays tend to approach the same direction, *i.e.*, along the air base. With the radial-stereoplotter it is possible to plot accurately the positions of the principal points themselves, but between them is a sort of lune within which points cannot be plotted with precision. This figure covers the area where the angle between the radial arms is 150° or greater.

Description of the Radial-stereoplotter

General

With the aid of the foregoing somewhat abbreviated explanation of the principles of the plotter, it will be possible to follow its construction. The main problem in design was to provide a number of sliding members without introducing backlash on the one hand, or, on the other, forces of sufficient magnitude to limit the free working of the machine or to strain any part to the extent that the accuracy would be impaired. This latter consideration, while to some extent self-evident, had been emphasized in some investigations on factors affecting the precision of first-order theodolites, carried out at the National Research Laboratories a short time ago (4).

The problem was met by constructing all moving parts as light as possible, and employing ball bearings to act as rollers at many of the sliding contacts. One also attempted to reduce the arms of couples to a minimum. When the machine had been constructed it was found that these efforts, coupled with the first-class workmanship contributed by the Instrument Shop, had been successful to the extent that operation is exceedingly free and smooth, with imperceptible backlash.

The machine is illustrated in Figs. 4, 5, 6 and 7. In Fig. 4 the complete plotter is shown, Fig. 5 is a view with the upper and lower carriages removed, Fig. 6 shows the lower carriage, bearing the stereoscope (seen from one end), and Fig. 7 is an underneath view of the upper, plotting carriage.

Two tables *A* (Figs. 4 and 5), mounted on pivots with centres 18.5 in. apart, hold the photographs. These tables can be clamped, released, and rotated freely by hand, or rotated slowly by screws *B*, acting on the clamping screws *C*, following somewhat the system used in transits. Fine needle holes indicate the centres of rotation of the tables, and spring clips serve to hold the photographs in place. This portion of the machine follows lines that have been successfully applied to simple stereoscopes designed for government survey offices at Ottawa.

The right-hand print table can be moved in a direction perpendicular to the base for the purpose of measuring want of correspondence in this direction. This is accomplished by mounting the pivot housing in slides, with gib and screws for taking up slackness. Movement of the table is controlled by a screw butting against the front of the housing and a spring and plunger at the rear. A scale and vernier measure displacements, and permit the table to be reset for plotting purposes.

An I beam, on its side, is used to support the main pivot bearing housings for the radial arms (E, Fig. 3). These bearings are also spaced at 18.5 in. centres and each consists of two torque-tube ball bearings, $2\frac{5}{16}$ in. bore. The radial arms are located by keys cut out of the solid ends of the pivots and are ground parallel. The centres of the pivots and of the tables are adjusted so that their horizontal projection forms a rectangle. This, as well as all the other adjustments necessary to secure accurate working, can be made directly by observations carried out with the aid of the stereoscope telescopes or other parts of the plotter. Adjusting screws are provided for bringing the different slides into parallelism and otherwise correcting the various geometrical relations of the elements of the machine to secure accurate performance.

Lower Carriage

The lower carriage, Fig. 6, is supported on three rollers, consisting of commercial ball bearings fitted on eccentric pins to permit adjustment. It is guided in the Y direction (*i.e.* perpendicular to the air base) by four similar rollers D, which engage with the sides of a fixed, rectangular section bar carried on a light I beam E (Fig. 5), and which also forms a rail for the central supporting roller of the carriage. The body of the carriage is an aluminium casting and is moved in the Y direction by means of a screw F. A sliding piece G, carried on two bars parallel to F, is fitted with a half nut which can be engaged with F or released by an arm H, linked to a lever J (Fig. 6) conveniently located at the end of the carriage. The coupling between G and the carriage is a strut fitted with spherical ends so that direct pull or push forces only can be transmitted.

The screw F is coupled to a handwheel, placed conveniently at the observer's right hand, by means of the shafts and bevel gears seen in Fig. 5, and which are mounted in ball bearings, with ball thrust for the screw, to permit smooth, easy operation of the carriage to its final setting during an observation.

The stereoscope may be considered as composed of three parts, mounted on two thin-walled steel tubes K and L (Fig. 6). The central portion, fixed to the middle of the tubes, bears the two telescopes. Optically, each telescope consists of an objective (25 mm. diam.), two prisms to erect the image and present it to the eye at a comfortable inclination (20° above horizontal), a glass diaphragm ruled with one-half the floating mark and an eyepiece giving a magnification of about $2.5\times$. The objective is mounted in a sleeve, focused by means of a nut, M, engaging with two portions of a screw fitted in slots on the telescope tube 180° apart. The eyepieces can also be focused and their spacing varied to suit individual observers. This latter adjustment is made by a right- and left-handed screw, and, when it is completed, clamping screws enable the telescopes to be clamped firmly on the slide carrying them.

Stainless steel mirrors, N, 50 by 50 mm., each spring-constrained against the points of three adjusting screws, are held on the two outer brackets of the stereoscope, which also bear the pivots corresponding to B and B_1 (Fig. 3). These pivots consist of spindles each carried in two self-aligning ball bearings,

and fitted at its upper end with a triangular plate of duralumin on which are mounted three horizontal rollers (non self-aligning ball bearings). Eccentric pins are used to carry these rollers so that the axis of rotation of the pivot can be made to coincide with the axis of rotation of the lower radial arm with which the rollers engage. By adjustment the telescope diaphragms are brought to focus on points at the same spacing as the axes of the pivots, thus conforming to the relations illustrated in Fig. 3. Adjustment of this spacing (parallax change) is effected by means of a right- and left-handed screw, parallel to and placed between the tubes K and L. A quadruple-threaded wormwheel at the centre of this screw, mounted in the central bracket of the stereoscope assembly, engages with a worm on the same shaft as the handle O (Fig. 4). The right-left screw is cut with a vee thread, and the nuts on the outer brackets are split, so that these brackets, which are fitted with lapped bushings for the tubes K and L, slide along the tubes without back-lash or the necessity of any clamping device, which, indeed, would introduce difficulty owing to the frequency with which changes in parallax settings have to be made.

Slow movement of the stereoscope as a whole in the X direction on the carriage is controlled by a screw with a disengaging half-nut on the central bracket, linked to the small lever P (Fig. 6). The gearing and quill seen at the end of the carriage in Fig. 6 permit the screw to be operated from a shaft with handle set at the observer's left hand. The quill transmits a torque only, so that non-alignment of the shaft does not introduce friction.

Motion of the stereoscope in the X direction is governed by a slide, Q, made for convenience in grinding, from two pieces, and carried on brackets mounted on the rear of the carriage. Extensions on the mirror brackets carry rollers R which engage with the two opposite ground faces of this slide, which is placed as closely as possible to the plane of the lower radial arms. The weight of the stereoscope is supported by two rollers beneath each of the mirror brackets, and it was found necessary to mount a small roller under each bracket, at the rear, to resist a lifting tendency when the machine was operated.

Graduated scales are provided for indicating the change in spacing between the mirror brackets (parallax)—which can be read to 0.02 mm. by means of a vernier—the displacement of each mirror bracket in the X direction, and the displacement of the carriage in the Y direction; these latter scales can be read to within 0.1 mm. Lenses mounted in front of the verniers permit the scales to be read comfortably from the observer's seat.

A constant illumination of the portion of the picture covered by the field of view of the stereoscope (65 mm. diameter) is obtained by mounting an automobile headlight bulb on each mirror bracket.

Upper Carriage

The upper, or plotting carriage, is simpler than the lower one. It is like-wise a light aluminium casting and is supported on four rollers running on two rails, S (Fig. 5), carried on brackets bolted to the I beam flanges. Two

additional brackets, at the centre of the beam, are mounted with horizontal rollers in which engages the parallel bar T (Fig. 7), rigidly attached to the bottom of the carriage, and serving to guide the motion in the Y direction. The upper radial arms engage with rollers carried on pivots similar to those used in the lower carriage, and housed in light castings fitted to two thin-walled steel tubes. The right casting is fixed to the tubes, while the left one can slide to alter the spacing, *i.e.*, set the plotting scale of the Zeiss parallelo-gram. This setting is made by a screw above the tubes, the right end of which fits in a journal bearing on the casting, while the left end threads in a split nut, which can be clamped when the setting is made. A scale and vernier indicate the inset, or base length, in millimetres (*i.e.*, the length PE in Fig. 2). Each casting is supported on two rollers, running on ground steel rails, as in the case of the lower carriage, and the X direction guides, seen in Fig. 7, are also similar.

One of the steel tubes extends through the end of the carriage, and to it is attached a light truss bearing the plotting point. The plotting pencil, at the lower end of this truss, was made to fit on a slide with a rack and pinion to adjust the pencil by aid of a scale and vernier. This arrangement was to permit plotting with the centre of either photograph table as origin, but in practice it has been found best always to use the right photograph.

A table, fitted in a pivoted support with a clamping screw, serves to hold the paper. This is used in the form of a roll, the unused portions being held in light brackets beneath the table. Spring clips hold the paper in position during plotting. The plotting table is placed conveniently to the observer's right, and is visible in Figs. 4 and 5.

Experience would indicate the desirability of fitting a sighting microscope, for use in place of the pencil, when adjusting the plot to the photographs.

Method of Plotting Control with the Radial-Stereoplotter

(a) Photographs are set by centering the floating marks in turn on the engraved crosses that mark the centres of rotation of the photo-carrying tables, and then placing the photograph principal points under the floating marks.

(b) The photographs are oriented along the line joining their principal points, which will hereafter be called the base line. This is done by observing points of detail near each principal point in turn, and rotating the other photograph until vertical parallax disappears. The instrument gives a sensitive determination of vertical parallax (or want of correspondence), owing to the form of its floating mark. The forms of the marks are as shown in Fig. 8, a. Observed stereoscopically, the vertical lines fuse, and, when there

Left mark   Right mark
(a)   (b)   (c)

FIG. 8.

is no vertical parallax present in the plastic model (stereogram) against which the mark is viewed, the whole looks like a solid cross (Fig. 8, b). When there is any vertical parallax in the plastic model, the cross breaks up, and the horizontal lines appear separated in the Y direction (Fig. 8, c).

(c) The scale of the plot depends upon the ratio of the base-length (set on the upper carriage) to the natural distance between the objects on the ground on whose images the principal points of the photographs fall. If two points, whose distance apart is known, appear in the first overlap, the machine may be set to plot at any desired scale by first plotting the two points from the photograph with an arbitrary base-length setting. The arbitrary setting, B_1, is then corrected by multiplying it by the factor Dt/Dp, where Dt is the true distance at the desired scale, and Dp is the distance plotted at the first setting.*

(d) The machine works most conveniently when the plot proceeds from right to left of a series of photographs. When the scale has been set by adjusting the base-length as in (c), two minor controls or scale control points are plotted. These should lie on a line at right angles to the base line, at a distance equal to the base above and below the left principal point. If there happens to be want of correspondence, owing to tilt, at these points, the arms of the cross constituting the floating mark will not appear collinear. When plotting the two scale control points, care must be taken to have the right arm of the cross in line with the right photograph image of the point of detail chosen, since we are performing a radial line intersection, and the angle between the line from the object to the principal point and the base line on the *right* photographs determines the Y co-ordinate of the plotted position.†

(e) The left principal point and the base line are plotted, and the base line on the plot is prolonged in both directions to the limit of the machine's movement.

(f) Points that are required as additional control for the subsequent tracing of detail are now plotted.

(g) When work with the first overlap is completed, the second photograph is transferred to the right photograph carrier, and the third photograph placed on the left one. The pair is then oriented as in (b) and the base lines ruled in.

(h) The plot is shifted so that the plotted principal point of the second photograph now lies on the centre of rotation of the plotting table, where the pencil rests when the floating mark is centered over the centre of rotation of the right photograph carrier. This is the origin for plotting in each overlap.

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* *The base line is marked on each photograph by laying a straight-edge on stops which bring it exactly over the centres of rotation, and scoring lines with a needle point. This operation must be very carefully performed, since the azimuth of the strip depends on its accuracy, as will appear later. Accuracy may be easily checked by removing the straight-edge and moving the stereoscope along the base line, when the floating mark will show any deviation of the scored lines. The base lines are extended in both directions to the margins of the photographs.*

† *The point is identified by centering a piece of celluloid with a fine cross over it. The marker is fastened down by transparent adhesive tape. As the points are viewed stereoscopically in plotting successive overlaps, it is necessary only to identify them in this way. The actual plotting should be of the untouched point of photographic detail, as any attempt to mark it by pricking, pen, or pencil leads to loss of accuracy.*

(i) The plot must now be oriented. Regarding the successive base lines as the legs of a traverse, the angles between them will be shown on the photographs by the scored lines. We are now concerned with the angle between base 1–2 and base 2–3; this is shown on Photograph 2, and may be plotted. The plotting table is rotated through the appropriate angle, so that when the floating mark is placed on the prolongation of base line 1–2 on the plot the plotted base falls under the pencil point.

(j) It is now necessary to adjust the base-length so that the plot of the second overlap will be at the same scale as that of the first. This is done by setting the floating mark on one of the scale control points. If there is want of correspondence, the left arm of the floating mark must be in line with the left photograph image of the control point; for the same reason, *mutatis mutandis*, as given in *(d)* above. If the pencil now falls on the point as plotted from the previous overlap, the scale is correct. If there is a discrepancy, the base-length is altered until the pencil falls on the point.

(k) The scale is checked by plotting the other scale control point. If it plots in the same position as determined from the previous overlap, this proves the scale to be correct. Sometimes, however, there is a discrepancy, which may be due to some of the operations previously described not having been done with sufficient accuracy. These are checked, and if the discrepancy persists, it is due to the effect of tilt, combined with height differences, or distortion of the photograph materials. It may be observed that the instrument indicates clearly when relative tilt is present, by the want of correspondence (vertical parallax) shown by the floating mark; the magnitude and direction of tilt may also be deduced approximately.

Errors

The sources of error in plotting with the instrument, and by the radial line method generally will now be discussed, and methods will be suggested for eliminating them, or correcting the plot.

Sources of Error in Radial Line Plotting

In making a radial line plot of a series of aerial photographs, we are in effect making a graphical triangulation, using the angles between objects as shown on the photographs. The errors of the plot may be either in azimuth, or in scale, or in both. There may be an error in one azimuth angle, or a series of small errors having a cumulative bending effect on the chain of triangles; and there may be a change of scale in one overlap or a gradual change of scale, the cumulative effect of small inaccuracies. Sudden changes in azimuth or scale can be due only to mistakes, and can be detected by a simple check. The cumulative effects of small inaccuracies become apparent when the plotted strip is laid down in a compilation with the plots of adjoining photograph strips. If there are two ground control points in each end overlap of the strip, as is usually the case when control is by traverse, it is easy to determine whether a constant scale has been preserved throughout the length of the strip.

Azimuth Errors

Small errors in azimuth may be caused by:—

(a) Inaccurate centering of photographs on the carriers. The base line on the photographs will not be parallel to the base line as plotted.

(b) Inaccurate centering of principal point on plot on the centre of rotation (origin of plotting) of the table.

(c) Inaccurate orientation.

(d) Inaccurate ruling of principal point bases.

(e) Inaccurate setting off of change of azimuth on plot.

Errors due to perspective distortions in tilted photographs will be discussed later; their effects in flattish country, when tilts are less than 3°, are negligible.

The above sources of error can be largely eliminated by care on the part of the operator. The magnification of the photograph image, and the apparent magnitude of the floating mark, are such that it is possible to set the photograph in place to an accuracy of 0.03 mm.; base line orientation should be accurate to less than two minutes of arc. The thickness of the base lines scratched by needle point is about 0.10 mm., and any departure from straightness may be detected by moving the floating mark in the X direction over the *p.p.* base.

Errors *(b)* and *(e)* depend on the accuracy with which the pencil point can be placed over a previously drawn line. The thickness of the pencil lines is about 0.10 mm. With the aid of a magnifying glass, the pencil may be set to about this degree of accuracy. It is likely that the setting could be improved if a magnifying optical sight were available to replace the pencil for the adjustment, as in some continental plotting machines.

Experience shows that plotting by the machine holds azimuth accurately, as a rule, in flattish country. Long straight roads or railways, extending through several photographs, preserve their alignment. More difficulty has been found in keeping the scale constant throughout a strip; in many that were plotted in the early stages, variations of 0.025 between the beginning and end of a strip were found. Such errors are shown up by scaling on ground control at the ends of the strips, and by the fact that there are discrepancies between the positions of tie points plotted from adjoining strips. The same sort of errors have been met with in radial line plotting by ordinary graphical methods, and it was in the hope of eliminating these, and lessening the amount of adjustment necessary during compilation, that the radial-stereoplotter was devised.

Scale Errors

The scale is preserved, from overlap to overlap, by plotting the position of two lateral scale control points (minor control points) in one overlap, and then adjusting the base length of the succeeding overlap so that these points are plotted in identical positions. The accuracy with which this process can be carried out depends on the following factors:—

(a) Accurate identification, from overlap to overlap, of the points of detail serving as scale control points.

(b) Definition and magnitude of the points of detail.

(c) Accuracy of pointing from the principal point to control point: *i.e.*, accuracy of measurement of the angles used for intersection and resection.

(d) Accuracy of orientation, and fineness of the setting of the plotting pencil.

The effects of tilt on the preservation of scale will be discussed later.

An important advantage of the radial-stereoplotter is that the direction lines are fixed when the operator observes the images of the control points in both photographs stereoscopically. This eliminates the errors in identification, which occur when points in successive photographs are established by inspection. The next factor in securing accuracy of pointing is the definition of the point of detail. Artificial detail, such as the intersections of roads, corners of buildings, etc., is best; but much Canadian mapping is of areas where there is no artificial detail, and natural objects such as trees, rocks and so on, seldom show as sharply as one would wish. The operator must take care to choose an object on which he can point to within 0.10 mm. or less, if at all possible.

It is best not to actually mark the object by pricking or in any other manner, as this spoils the stereoscopic impression, as explained above. If the foregoing precautions are observed, it is possible to make pointings to an accuracy of 0.1 mm. or less.

If the floating mark is not brought to exactly the same parallax as the photograph image, the discrepancy in X is reproduced in the Y direction. It is, therefore, necessary to be careful in making coincidence; if want of correspondence is present, it should be eliminated by the differential Y motion of the right photograph carrier; after the floating mark is adjusted to the correct parallax, the difference in Y is restored, as pointings would otherwise be incorrect to any objects not on the ordinate through the right principal point.

With the usual conditions applying to Canadian air surveys—scale control points about 70 mm. from the principal point and a camera focal length of 210 mm.—an error of 0.1 mm. in plotting the scale control points will introduce a scale error of 1/700 or 0.0014. Unless the operator has some idiosyncrasy in pointing, the errors will be random, and tend to cancel out. A strip that showed a total scale change of more than 0.005 from one end to the other would, if reduced according to its over-all scale, put control points towards the centre out of position by about a millimetre—53 ft. at the usual scale of plotting, which is 1/15,840. While errors of this magnitude would not matter in mapping certain types of country, it is desirable to be able to eliminate them when greater accuracy is desired. In such a case, the strip would have to be plotted again; or a special adjustment made to correct for the effect of the scale variation.

The Effect of Tilt in Flat Country

If we take the case of three photographs of flat country, numbered 1, 2 and 3, of which 1 and 3 are untilted, and 2 is tilted to the right in the direction of the base line, the condition would be as shown in Fig. 9. V_2 is
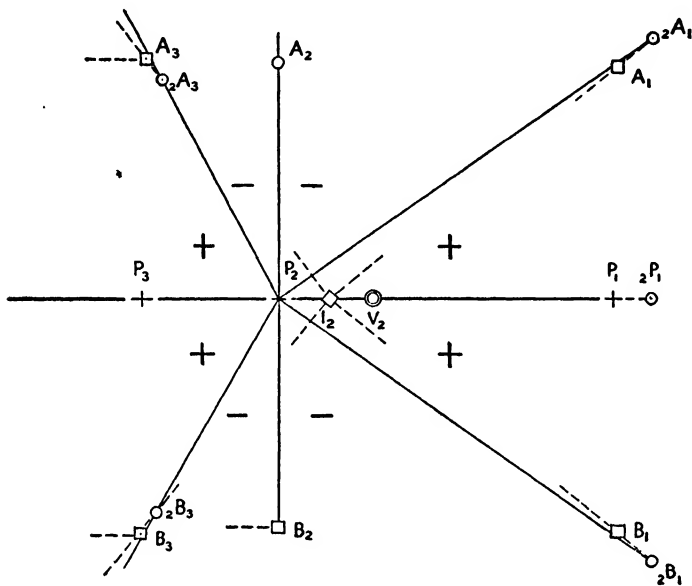
FIG. 9.

the plumb point of the second photograph, and I_2 its isocentre. Angles about its principal point will not be true. If the isocentre, I_2, could be found and used as the centre of plotting, angles would be true, but it is not practicable to do this.

It will be seen that the angles $_2A_1P_2P_1$ and $_2B_1P_2P_1$, and also $_2A_3P_2P_3$ and $_2B_3P_2P_3$ are larger than they should be. The ratio of the tangents of these angles to the tangents of true plan angles is sec θ, where θ is the tilt (3, Art. 17). The complementary angles will be too small, and in Fig. 9 a plus or minus sign has been placed to indicate the tilt effect on the angles in each of the eight sectors into which the photograph is divided by lines drawn to the surrounding control points.

It is clear that if the strip is oriented along the base lines there will be no error in strip azimuth; but a difference of scale will be introduced.

As the angles between A_1, and P_1 and B_1 are too large on photograph 2, when the position of P_2 is determined by resection it will be too close to P_1. The ratio of the plotted base line P_2P_1 to its true length will be cos θ. When A_2 and B_2 are intersected, the scale along A_2B_2 will be too small (in the same ratio) as it depends on the base P_2P_1; when P_3 is resected, the base P_3P_2 will be short, since it has been established from the line A_2B_2, which is short. But A_3 and B_3, which are intersected by the angles $A_3P_2P_3$ and $B_3P_2P_3$, which are too great, will be in their correct position and the scale will be re-established.

Tilts in gyropilot-controlled aircraft are seldom as great as 3°, and if the cosine of 3° is applied to 70 mm., the average base length is shortened by only 0.10 mm., a negligible amount, practically speaking.

If a line with an occasional larger tilt had to be plotted, the magnitude and direction of the tilt could be estimated (2, pp. 140–147), and after resection from the photograph, the base length could be increased by the amount required.

Inspection of Fig. 9 will show that if the direction of tilt were transverse to the line of flight, the angles with which resection and subsequent inter- section are made would be too small, and the base lengths and scale generally in the two overlaps in which the tilted photograph figured would be too large, coming back to normal with the next untilted pair.

If the direction of tilt is at 45° to the base line, one of the resection angles will be too great, and the other will be too small. The position of P_2 will not be properly resected unless allowance is made for this, and the pointing to the photograph detail is slightly varied accordingly. There will be no error in azimuth introduced. This case of tilt is the most troublesome in practice.

Tilt and Elevation Differences

Fig. 10 is a diagram of the plan position of the principal points of three photographs, the centre one of which is tilted laterally. V_2 is its plumb point. If the point of detail upon which P_1 falls is higher than the plotting
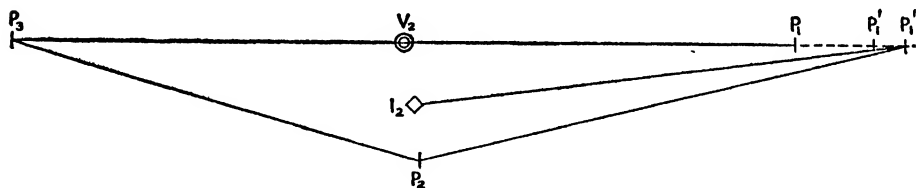
FIG. 10.

datum plane, its position will be distorted outwards to P_1'. Tilt will cause the principal point to move to P_2, and P_1' will move to P_1'' on a line radial from the isocentre. The line P_2P_1'' will therefore not give the true direction to the plan position of P_1 relative to other objects imaged in the photograph, and this discrepancy, the magnitude of which may be easily calculated, will seriously disorient the strip.

In such a case the trouble will soon show itself. The tilt will be indicated by want of correspondence; and its direction and magnitude, and hence the approximate plumb point, can be estimated by methods described by Major Hotine (2).

The overlaps where the difficulty occurs could then be plotted again, by use of the approximate plumb points so found, instead of the principal points.

Results Obtained with the Instrument

At the date of writing, the radial-stereoplotter has been in use for only about two months. Most photogrammetric machines can, in a special test, be made to give an output and accuracy beyond what would normally be obtained in routine mapping with them. On the other hand, when a new instrument is brought into use, operators gradually acquire skill with it and increase their output. It is, therefore, not possible to state finally to what degree the radial-stereoplotter will increase the accuracy and speed of radial line plotting. However, experience to date indicates that when plotting at 1/15,840 (4 in. to 1 mile) azimuth can be held correct in strips of photographs where the tilt is small so that the centre of a strip 750 mm. between ground control points will not be bent laterally by more than 1 mm. The scale can be held correct to about 1% from one end of the strip to the other.

In plotting a strip by machine, about 18 to 19 min. per photograph is required, including the plotting of roads and other subsidiary control for tracing. The experience in the Geographical Section, General Staff, has been that by the graphical method about 25 min. per photograph was required, time taken for plotting roads, etc., not included.

When strips are plotted to the accuracy mentioned above, an appreciable amount of time is saved in reduction, adjustment, and compilation, which, with the ordinary graphical method of plotting, takes about 16 min. per photograph.

Acknowledgments

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THE REFRACTIVE INDICES OF LIQUID OXYGEN, NITROGEN, AND HYDROGEN[1]

BY H. E. JOHNS[2] AND J. O. WILHELM[3]

Abstract

The refractive indices of liquid oxygen, nitrogen, and hydrogen at temperatures ranging from the normal boiling point to the normal freezing point of the liquefied gases were determined by means of a Wollaston cell for the wavelengths 6939Å, 5461Å, and 4358Å. The values obtained at the normal boiling point for $\lambda = 5461$Å were: oxygen, 1.2242; nitrogen, 1.1990; hydrogen, 1.1120.

This research was undertaken with the purpose of measuring the refractive index of liquid helium I and II in an effort to throw additional light on the nature of helium II. As yet no final results have been obtained for helium, but in perfecting the apparatus new determinations have been made for oxygen, nitrogen, and hydrogen. Heretofore a complete set of data has not been available for these liquids, as only isolated measurements have been made in the past.

In 1891 Olszewski and Witrowski (8) found the refractive index of oxygen, at the normal boiling point, to be 1.2222 for the sodium D line. The following year Dewar and Liveing (3) obtained the value 1.226, and in 1893 worked out a dispersion curve, this time determining the index as 1.2214 (5). Dewar and Liveing (4) also made measurements on nitrogen at the normal boiling point and obtained the value 1.2053 for the index. In 1901 Dewar (2) found the value 1.12 for hydrogen by the apparent depth method.

In this research the refractive indices have been determined for three different wave-lengths at temperatures ranging from the normal boiling point to the normal freezing point of liquid oxygen, nitrogen, and hydrogen.

Experimental

An evacuated Wollaston cell was used by means of which the critical angle from the liquid to vacuum could be obtained, and hence the refractive index. The cell was constructed from two circular, plane polished pieces of Pyrex about 1 mm. thick and 3 cm. in diameter, sealed together around the edge by heating, leaving an air space of approximately 0.1μ. Through the skilful

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efforts of Mr. R. H. Chappell a cell was produced that was practically free from distortion. The space between the two glass plates was then evacuated and the cell, *J*, mounted as shown in Fig. 1.

The liquid under consideration was placed in the flask *B* and light from a broad monochromatic source was passed through the flask and cell. The light was examined with a telescope focused for parallel light. When the cell was placed at the critical angle, the field of view of the telescope was divided into sharply defined bright and dark portions. Because the cell was so very thin, interference fringes were formed in the vacuum space, and were observed in the telescope when the cell was placed near the critical angle. In taking readings the cross hair was always set on the outermost fringe, which divided the bright and dark portions of the field of view.

Fig. 1 shows the specially designed Pyrex flask, which consisted essentially of two vacuum flasks, *A* and *B*, so separated that liquid air might be kept between them to protect the liquid hydrogen or helium in the inner flask. The inside flask was made with parallel plane faces, and plane windows, *C*, were inserted in the outer flask. These flasks were joined at *D* and *E* in such a way that light did not have to pass through the liquid air. The common vacuum space surrounding *A* and *B* was maintained by a pump attached at *O*. The top of the flask was fitted with a German silver cover, *F*, into which was soldered the stuffing box, *G*. A $\frac{1}{2}$ in. German silver tube extending almost to *J* was attached to *G*. The cell was suspended from a $\frac{3}{16}$ in. German silver tube and this in turn from a brass rod, *K*, which could be turned in the stuffing box, *G*. By placing three circular guides in the outer German silver tube the long suspended rod could be rotated accurately about a vertical axis.
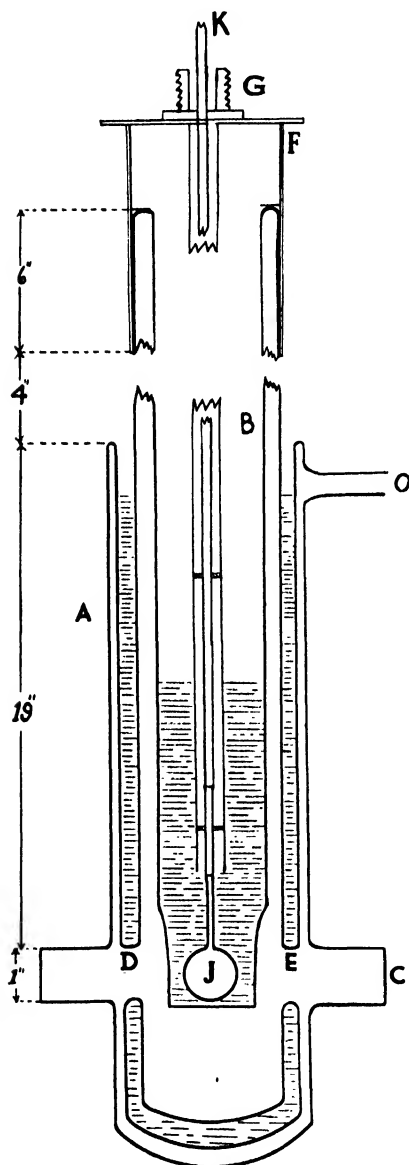
A divided circle with a fixed vernier was attached at *K* so that the angle

FIG. 1. *Diagram of apparatus.*

through which the cell was turned could be measured to the nearest minute. A flexible steel cable 5 ft. in length was connected to the slow motion screw so that the cell could be turned slowly to the critical position by an observer looking through the telescope at C. By turning the cell to four symmetrically placed positions, two values were obtained for each critical angle.

Difficulties were encountered in keeping the vernier from creeping slightly, as well as in making the cell rotate accurately about its vertical diameter. The apparatus had to be extremely rigid to prevent movement of the cell when the pressure in the inner flask was altered. In the measurements with the potassium red line, 6939 Å, it was difficult at times to obtain sufficient illumination and to keep out extraneous light. The most difficult problem, however, was to obtain a cell that was free from distortion. It was found that the measured critical angles differed on the two sides of the cell owing to the fact that the plates of glass were slightly prismatic, and that the measured angles varied slightly for different parts of the cell. The cell that was finally used gave two values which agreed to within three minutes. This cell was also checked with water. It gave the value 1.3346 as compared with the value 1.3342 as given in the International Critical Tables for water at 23° C. and light of wave-length 5461 Å. This difference corresponds to an error of one minute in the critical angle.

Results

The results obtained are given in Tables I, II, and III, and are represented graphically in Figs. 2 to 7. The values given in the tables are only those that were obtained under the best experimental conditions.

TABLE I

THE REFRACTIVE INDICES OF LIQUID OXYGEN BOILING AT DIFFERENT TEMPERATURES

Temp., ° K.	Density, gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$	Temp., ° K.	Density, gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$
$\lambda = 4358$ Å				$\lambda = 5461$ Å—*Continued*			
90.3	1.1425	1.2277	0.1448	83.7	1.1742	1.2308	0.1465
90.0	1.1435	1.2283	.1450	82.2	1.1815	1.2322	.1473
89.1	1.1485	1.2293	.1456	80.5	1.1898	1.2345	.1487
87.6	1.1555	1.2311	.1467	76.9	1.2070	1.2369	.1501
85.5	1.1655	1.2328	.1477	73.8	1.2218	1.2401	.1520
83.6	1.1747	1.2345	.1487	69.7	1.2415	1.2442	.1544
82.4	1.1805	1.2355	.1493	65.0	1.2640	1.2483	.1569
79.8	1.1931	1.2382	.1509				
76.9	1.2070	1.2416	.1529	$\lambda = 6939$ Å			
73.6	1.2228	1.2446	.1547	90.3	1.1425	1.2226	0.1416
69.7	1.2415	1.2483	.1569	90.0	1.1435	1.2233	.1420
65.0	1.2640	1.2518	.1590	87.5	1.1560	1.2258	.1435
				87.3	1.1570	1.2262	.1437
$\lambda = 5461$ Å				87.1	1.1577	1.2263	.1438
90.3	1.1425	1.2243	0.1426	83.7	1.1742	1.2293	.1453
90.0	1.1435	1.2241	.1425	79.8	1.1931	1.2330	.1478
89.1	1.1485	1.2251	.1431	77.0	1.2063	1.2347	.1488
87.6	1.1555	1.2271	.1443	73.8	1.2218	1.2382	.1509
86.5	1.1607	1.2276	.1446	69.7	1.2415	1.2417	.1530
85.6	1.1650	1.2295	.1457	65.7	1.2609	1.2441	.1544
85.4	1.1660	1.2293	.1456				

Oxygen

The results for oxygen are given in Table I and are shown graphically in Figs. 2 and 3. Points marked by circles and dotted circles refer to readings taken during two separate experiments. Fig. 3 shows $\mu^2 - 1/\mu^2 + 2$ plotted against the density which was obtained by Mathias and Onnes (6), and Baly and Donnan (1).
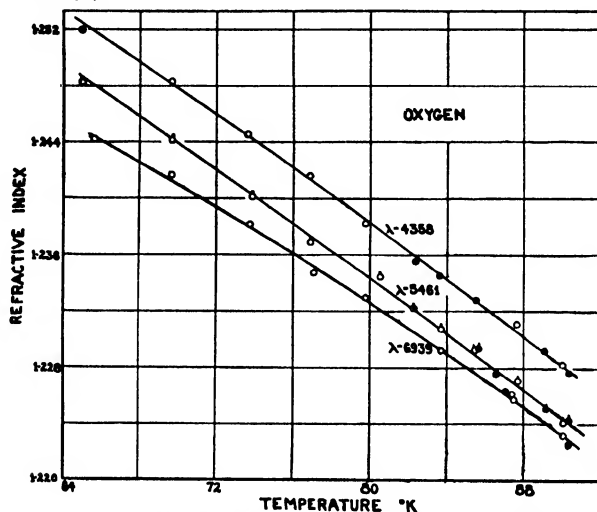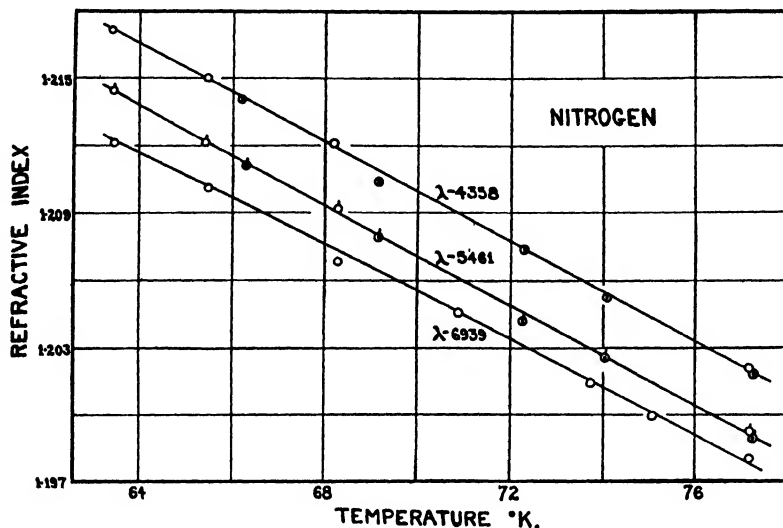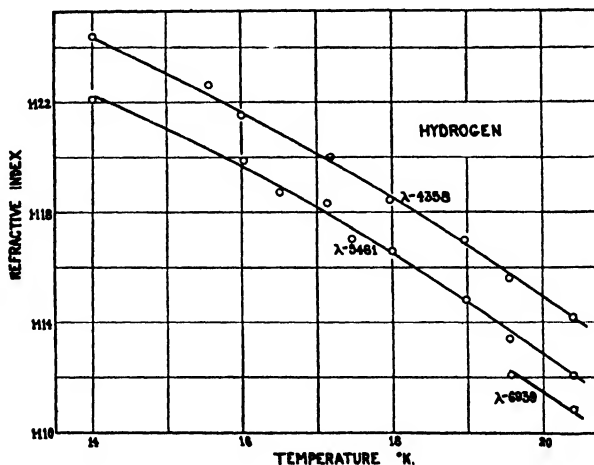

FIG. 2. *The temperature-refractive index diagram of liquid oxygen.*
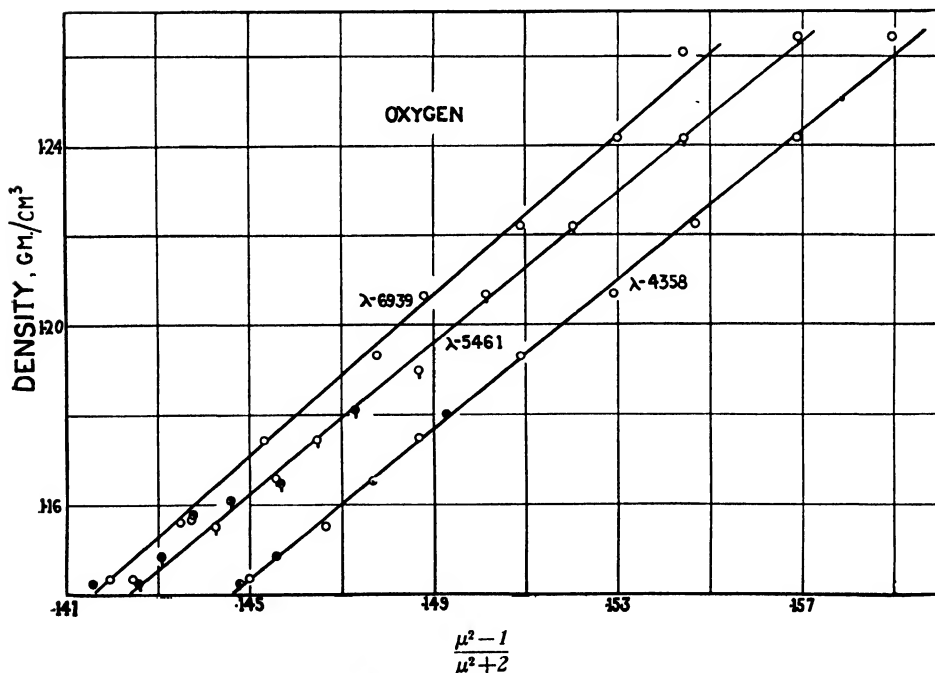
FIG. 3. *The function $\dfrac{\mu^2 - 1}{\mu^2 + 2}$ plotted against the density for liquid oxygen.*

The best values for the refractive indices of oxygen, at the normal boiling point 90.21° K., obtained from the graphs are: $\lambda = 4358$ Å, 1.2280; $\lambda = 5461$ Å, 1.2242; $\lambda = 6939$ Å, 1.2230.

An error of two minutes in the critical angle would introduce an error of ± 0.0005 in the value of the refractive index. As can be seen from the graph, few of the points deviate by more than this amount from the lines. It is possible that an error due to the interference fringes might have been introduced, for if the critical angle happened to come at a position of interference no line would be present to set on, and the second fringe would have been used. However, in all cases the cross hair was set on the outermost fringe even if it was faint. An error of $\frac{1}{4}$ fringe width introduces an error in the refractive index of 0.0002 for 4358 Å, 0.0003 for 5461 Å, and 0.0004 for 6939 Å. It is therefore likely that the errors in the present determinations are less than ± 0.0005. These values are higher than those of Dewar and Liveing, who obtained the value 1.2214 for the sodium D line (5). This difference corresponds to an error of 10 min. in the critical angle.

Nitrogen

The results obtained for nitrogen are given in Table II and are presented graphically in Figs. 4 and 5.

TABLE II

THE REFRACTIVE INDICES OF LIQUID NITROGEN BOILING AT DIFFERENT TEMPERATURES

Temp., ° K.	Density (7), gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$	Temp., ° K.	Density (7), gm. per cc.	Refractive index	$\frac{\mu^2-1}{\mu^2+2}$
$\lambda = 4358$ Å				$\lambda = 5461$ Å—*Continued*			
77.3	0.8078	1.2019	0.1291	68.3	0.8473	1.2092	0.1335
77.2	.8081	1.2021	.1292	66.3	.8563	1.2111	.1347
74.1	.8220	1.2053	.1311	65.5	.8592	1.2121	.1352
72.4	.8296	1.2074	.1324	63.5	.8677	1.2144	.1367
69.3	.8431	1.2104	.1342				
68.2	.8478	1.2121	.1352	$\lambda = 6939$ Å			
66.3	.8563	1.2140	.1364				
65.5	.8592	1.2150	.1370	77.2	0.8081	1.1980	0.1267
63.5	.8677	1.2171	.1383	75.1	.8176	1.1999	.1279
				73.8	.8238	1.2015	.1288
$\lambda = 5461$ Å				70.9	.8361	1.2045	.1307
				68.4	.8469	1.2068	.1321
77.3	0.8078	1.1990	0.1273	65.5	.8592	1.2101	.1340
77.2	.8081	1.1993	.1275	63.5	.8677	1.2121	.1353
74.1	.8220	1.2026	.1295				
72.4	.8296	1.2042	.1305				
69.2	.8435	1.2080	.1327				

The refractive indices for nitrogen at the normal boiling point, 77.38° K. (see graph), are: $\lambda = 4358$ Å, 1.2019; $\lambda = 5461$ Å, 1.1990; $\lambda = 6939$ Å, 1.1977.

As in the case of oxygen the results are not in error more than ± 0.0005. It can be seen from the graph that none of the points deviate by more than

this amount from the lines. Dewar and Liveing (4) obtained the value 1.2053 for the sodium D line with nitrogen at a temperature of $-190°$ C. The value that is given in the International Critical Tables for nitrogen at the normal boiling point is 1.1975 for 5790 Å, which is in fairly good agreement with that obtained by the authors.

FIG. 4.   *The temperature-refractive index diagram for liquid nitrogen.*
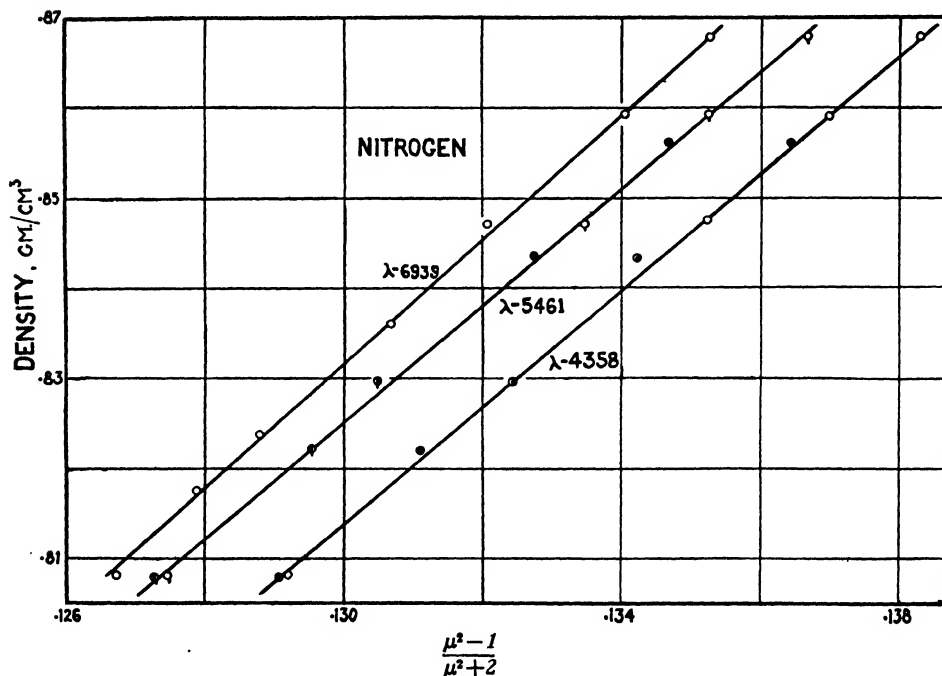
FIG. 5.   *The function* $\frac{\mu^2-1}{\mu^2+2}$ *plotted against the density for liquid nitrogen.*

Hydrogen

The results for hydrogen are given in Table III and are represented graphically in Figs. 6 and 7. Owing to the fact that the hydrogen became slightly cloudy at the lower temperatures a complete set of measurements could not be made for 6939 Å.

<div align="center">TABLE III</div>

<div align="center">THE REFRACTIVE INDICES OF LIQUID HYDROGEN BOILING AT DIFFERENT TEMPERATURES</div>

Temp., °K.	Density (9), gm. per cc.	Refractive index	$\dfrac{\mu^2-1}{\mu^2+2}$	Temp., °K.	Density (9), gm. per cc.	Refractive index	$\dfrac{\mu^2-1}{\mu^2+2}$
$\lambda = 4358$ Å				$\lambda = 5461$ Å—*Continued*			
20.39	0.07085	1.1142	0.07447	18.00	0.07338	1.1166	0.07601
19.56	.07175	1.1156	.07538	17.45	.07392	1.1169	.07620
18.96	.07239	1.1170	.07627	17.13	.07424	1.1184	.07716
17.97	.07341	1.1184	.07715	16.50	.07484	1.1187	.07735
17.22	.07415	1.1199	.07811	16.02	.07528	1.1199	.07811
16.01	.07529	1.1215	.07912	14.01	.07709	1.1221	.07950
15.58	.07568	1.1226	.07982				
14.01	.07709	1.1244	.08096	$\lambda = 6939$ Å			
				20.39	0.07085	1.1108	0.07232
$\lambda = 5461$ Å				19.56	.07175	1.1121	.07315
20.39	0.07085	1.1121	0.07315				
19.56	.07175	1.1134	.07398				
18.96	.07239	1.1148	.07487				

The best values for the refractive indices of hydrogen at the normal boiling point, 20.41° K., are: $\lambda = 4358$ Å, 1.1141; $\lambda = 5461$ Å, 1.1120; $\lambda = 6939$ Å, 1.1107.

An error of two minutes in the critical angle would introduce an error of ± 0.0003 in the value of the refractive index for hydrogen. As can be seen

FIG. 6. *The temperature-refractive index diagram for liquid hydrogen.*
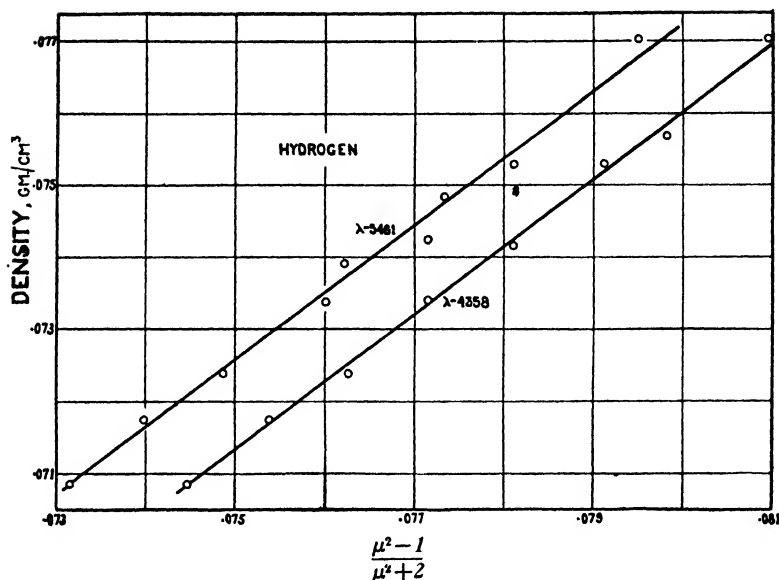
FIG. 7. *The function* $\dfrac{\mu^2-1}{\mu^2+2}$ *plotted against the density for liquid hydrogen.*

from the graph few of the points deviate by more than this from the line. It is therefore likely that the errors in these determinations are less than ± 0.0003. These values are low as compared with the value 1.12 obtained by Dewar (2), and high as compared with 1.097 as given in the International Critical Tables for 5790 Å.

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THE COEFFICIENT OF HEAT TRANSFER FOR VERTICAL SURFACES IN STILL AIR[1]

By R. Ruedy[2]

Abstract

For a vertical plane surface in still air the coefficient of heat transfer, valid within the range of temperatures occurring in buildings, depends on the temperature and the height of the surface. If black body conditions are assumed for the heat lost by radiation, the coefficient is equal to 1.39, 1.50, 1.62, and 1.73 B.t.u. per sq. ft. per ° F. at 32°, 50°, 68°, and 86° F. respectively, the height of the heated surfaces being 100 cm. Convection is responsible for about one-third, and radiation, mainly in the region of 10 microns, for about two-thirds of the heat loss. Convection currents depend on the temperature difference, while radiation depends on the average temperature. When attempts are made to stop convection currents by placing obstacles across the surface, the loss of heat due to natural convection varies inversely as the fourth root of the height, providing that the nature of the flow of air remains unchanged.

Introduction

Little attention is paid to the various factors contributing to the flow of heat when the heat lost through windows is measured. The form of the flow of heat becomes too complicated to be established by measurements alone, so that it is useful to study a relatively large vertical surface as a standard with which surfaces having cross bars and other obstacles may be compared.

The single window behaves like any other partition that is in contact with warm air of temperature t_n on the inside and with cold air of temperature t_e on the outside. In order that a steady transfer of heat may take place, appropriate temperature differences must establish themselves between (i) the mass of warm air and the inner surface of the window, (ii) the two glass surfaces, (iii) the outer surface of the pane and the atmosphere. Because the decrease in temperature across windowpanes is small, the transfer of heat between the air and the glass is most important, and is no longer a quantity for which an approximate value may be introduced, as in thick walls, without appreciably changing the results.

Natural Convection

The windowpane gains and loses heat by radiation and by natural convection. The cold air that is in contact with its outer surface is heated by the warmer glass surface, rises to the top of the window, and along the walls until it has lost the heat that it has gained. Near the bottom of the warm glass surface the difference in temperature between the glass and outside air is large and, hence, the air is heated rapidly.

When the windows and the walls are in practically the same vertical plane, and when the temperature differences are not too large, the flow of these convection currents obeys the equations for laminar conditions (6, 7):

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_y}{\partial y} = \nu \frac{\partial^2 v_y}{\partial x^2} + g\left(\frac{T}{T_e} - 1\right) = \nu \frac{\partial^2 v_y}{\partial x^2} + g\frac{T_w - T_e}{T_e}\theta$$

$$v_y \frac{\partial \theta}{\partial y} + v_x \frac{\partial \theta}{\partial x} = a\frac{\partial^2 \theta}{\partial x^2}$$

in which,

v is the velocity of the air at any point x, y,

T is the temperature (° K.) at any point x, y,

T_w is the temperature (° K.) of the wall,

T_e is the temperature (° K.) of the mass of outside air,

$\theta = \dfrac{T - T_e}{T_w - T_e}$,

g is the constant of gravity,

a is the diffusivity of the air,

ν is the coefficient of kinematic viscosity.

After the introduction of the independent variable

$$\eta = \sqrt[4]{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)} \frac{x}{\sqrt[4]{y}} ,$$

the solution of the system of equations may be expressed by two functions of η and their derivatives,

$$\theta = X(\eta) ,$$

$$v_y = 4\nu \sqrt{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)} \Gamma(\eta) .$$

The functions X and Γ are given by infinite series that satisfy the differential equations for the convection currents set up in the vertical direction y. The temperatures and the velocities, v_y, in a vertical direction, near a vertical surface kept at the temperature t_w, are plotted in Figs. 1 to 4, for three cases that often occur in practice.

The corresponding equations are,

$$v_y = 17\sqrt{y}\,\Gamma\left(5.5\frac{x}{\sqrt[4]{y}}\right) \quad t = 20\,X\left(5.5\frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{array}{l} t_w = 20° \text{ C.} \\ t_e = 0° \text{ C.} \end{array}$$

$$v_y = 12.2\sqrt{y}\,\Gamma\left(4.87\frac{x}{\sqrt[4]{y}}\right) \quad t = 10\,X\left(4.87\frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{array}{l} t_w = 0° \text{ C.} \\ t_e = -10° \text{ C.} \end{array}$$

$$v_y = 22\sqrt{y}\,\Gamma\left(6.77\frac{x}{\sqrt[4]{y}}\right) \quad t = 30\,X\left(6.77\frac{x}{\sqrt[4]{y}}\right) \text{ for } \begin{array}{l} t_w = 0° \text{ C.} \\ t_e = -30° \text{ C.} \end{array}$$

The curves obtained show that at any height, y, the vertical velocity, v_y, of the natural convection currents, increases rapidly with the distance in the first few millimetres from the wall. Near the bottom of the vertical surface the maximum velocity is reached within less than 3 mm. from the wall, and near the top, within less than 6 mm. Beyond these points the velocity of the natural convection currents decreases nearly as rapidly as it increased. When, therefore, two surfaces are placed face to face so as to leave an air gap between them, the convection currents will be disturbed more near the top of the gap than near the bottom. A large reduction of the velocity of the air currents in a gap takes place only when the two solid surfaces are set closer than about 1.25 cm. or as close as 0.5 cm., depending upon the height.

FIG. 1.   FIG. 2.   FIG. 3.
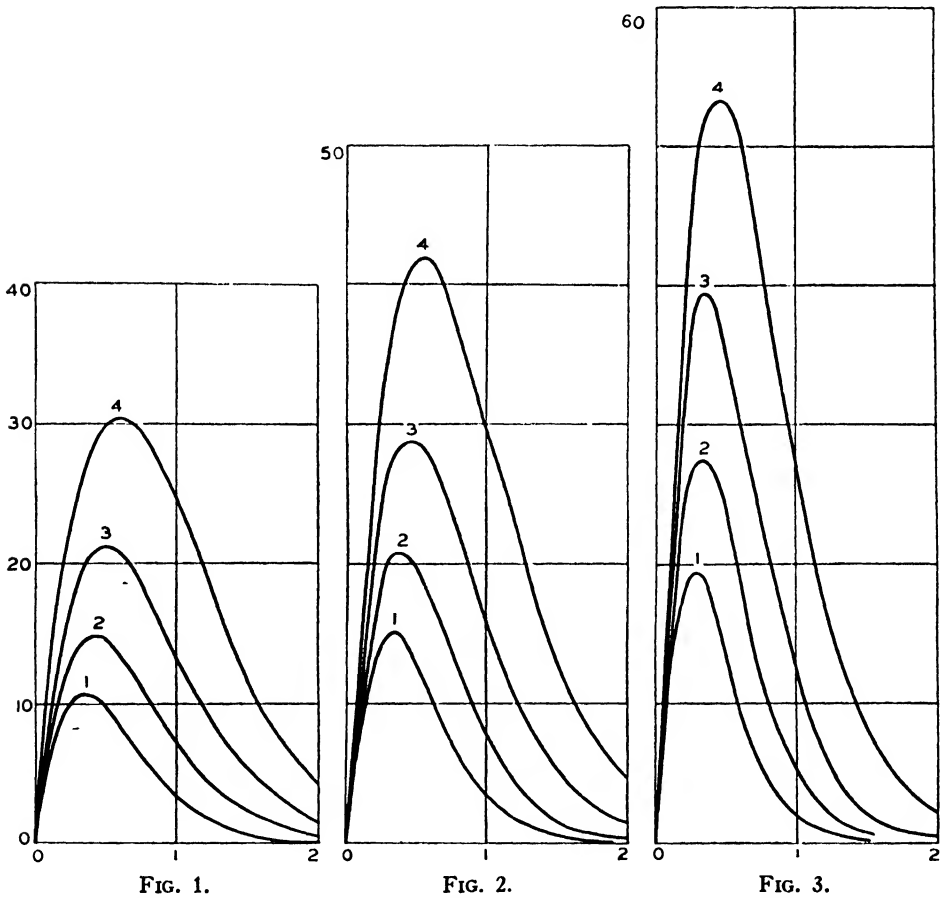
Vertical velocity (ordinates), in cm. per sec., of the convection currents at the distance x (abscissas), in cm., from a vertical wall heated in still air, and at four different heights y (10, 20, 40, and 80 cm., Curves 1, 2, 3, and 4). The temperature of the heated portion of the wall is t_w, that of the outside air, t_o.

FIG 1. $t_w = 0° C.$ FIG. 2. $t_w = 20° C.$ FIG. 3. $t_w = 0° C.$
$\quad\quad\quad t_o = -10° C.$ $\quad\quad\quad\quad\quad t_o = 0° C.$ $\quad\quad\quad\quad\quad t_o = -30° C.$

With increasing distance, x, from the surface, the temperature decreases quite rapidly at the bottom of the surface, and more slowly near the top; and, to within a few degrees, the outside temperature is reached at 1 cm. from the vertical surface. The increased loss of heat that natural convection produces may, therefore, be illustrated by comparing the loss due to convection with the heat conductivity of air, since this figure refers to a drop of one degree per unit length.

The transfer of heat per unit surface per unit degree difference in temperature ($t_w - t_e = 1$) is equal to

$$k = -\lambda \frac{\partial \theta}{\partial x} \quad \text{at } x = 0 \text{ (wall)}$$

or $k = -\lambda X'_w \cdot \sqrt[4]{\frac{g}{4\nu^2}\left(\frac{T_w}{T_e} - 1\right)} \frac{1}{y}$

at any point of the boundary. Integrating between $y = 0$ and $y = h$ and taking the average gives the value in Calories per square metre per hour per degree Centigrade,

$$k_m = -\frac{4}{3}\lambda X'_w \cdot \sqrt[4]{\frac{g}{4\nu^2 h}\left(\frac{T_w}{T_e} - 1\right)}$$

$$= 4.8 \sqrt{\frac{b}{760}} \sqrt[4]{\frac{T_w - T_e}{h\,T_e}}, \quad (1)$$

where b is the barometric pressure in millimetres of mercury, λ is the coefficient of heat conductivity of the air, and $X'_w = 0.021$.

The average surface coefficient is large when T_w/T_e is large and when the height of the warm surface is small. It is proportional to the fourth root of $(T_w - T_e)/T_r$ and inversely proportional to the fourth root of the height, h. The height, therefore, exerts a relatively small influence. The temperature enters into the formula for k not only as a function of the temperature difference between the walls and the outside air, but also as a function of the temperature of the outside air. For the temperatures likely to obtain near windows, $-50°$ to $+50°$ C., the temperature difference exerts the greatest influence as may be seen from Table I.

FIG. 4. *Temperature at heights 10, 80, and 120 cm. above the bottom edge (Curves 1, 2, and 3 respectively) at the distance x from a vertical wall heated in still air.*

TABLE I

VALUES OF $\sqrt[4]{\dfrac{T_w - T_e}{T_e}}$ FOR VARIOUS VALUES OF t_w AND t_e (° C.)

t_e, ° C.	t_w, ° C.					
	0	10	20	30	40	60
−20	0.530	0.586	0.636			
−10	0.442	0.525	0.581	0.625	0.660	
0		0.437	0.520	0.576	0.618	
10			0.433	0.516	0.571	0.648
20				0.430	0.511	0.615
30					0.426	0.561
40						0.503
						0.421

For the normal range within which Formula (1) is employed in practice the various other variables are given in Table II.

TABLE II

AUXILIARY VALUES

T_e, ° K.	$T_e^{-\frac{1}{4}}$	h, m.	$h^{\frac{1}{4}}$, m.	$t_w - t_e$, ° C	$\left(\dfrac{T_w - T_e}{T_e}\right)^{\frac{1}{4}}$
263	0.248	0.25	0.707	5	0.37
273	0.246	0.5	0.841	10	0.44
283	0.244	1	1	15	0.49
293	0.242	2	1.19	20	0.53
303	0.240	3	1.32	30	0.59
		4	1.414	40	0.63

The transfer of heat, H, in Calories per square metre per hour caused by natural convection is

$$H = \frac{4.8}{\sqrt[4]{h}} \sqrt[4]{\frac{T_w}{T_e} - 1} \ (t_w - t_e).$$

The tables show that as far as natural convection is concerned, the surface coefficient used in formulas of the type

$$H = \frac{kc}{\sqrt[4]{h}} \ (t_w - t_e)$$

becomes actually a function of the temperature difference only. For heights of one metre and temperatures between −20° and +40° C. the coefficients are given in Table III.

TABLE III

SURFACE COEFFICIENTS, k, DETERMINED BY NATURAL CONVECTION

Units	Temp. difference			
	5°	10°	20°	30°
Cal. per sq. m. per hr. per ° C.	1.76	2.12	2.55	2.84
B.t.u. per sq. ft. per hr. per ° F.	0.36	0.43	0.52	0.58

These coefficients should be compared with the thermal conductivity of air, in the absence of convection, namely 0.144, 0.156, and 0.168 B.t.u. per sq. ft. per hr. per ° F. at the temperatures 0°, 32°, and 100° F., respectively.

The fact that the heat carried away from a warm surface by natural convection varies inversely as the fourth root of the height was pointed out more than 50 years ago (3), and has been rediscovered from time to time (4). In an air gap the result obtained depends, however, on the width of the gap.

For a temperature difference of 50° F. across gaps 1.5 in. wide and 9 in. and 35 in. in height, the coefficients for both surfaces combined are 0.44 and 0.309 respectively (4). The ratio of the coefficients is 1.42; the fourth root of the inverse ratio of the height is 1.48. When the width is reduced to 0.8 in. the ratio of the coefficients is 0.42 : 0.28, or 1.50. The agreement remains satisfactory until spaces less than 0.4 in. wide are considered; with narrower gaps the ratio begins to decrease from the value 1.42 (that is, 0.47/0.33) toward unity. For gaps less than 4 in. in height the conditions outside the gap become as important as the height.

The theory used assumes that the heated surface is set flush into a large wall at uniform temperature, so that the air taking part in the convection arrives and leaves in laminar flow at the bottom and top. When the warm surface is freely suspended in a room the transfer of heat is greater, the coefficient 6.12 replacing the value $0.848 \lambda/\nu^{\frac{1}{3}}$, which is equal to 4.8 for all temperatures between $-50°$ C. and $+50°$ C. (8). A larger coefficient is probably also valid when the temperature differences increase and the flow becomes turbulent.

The resistance that the flowing air has to overcome in order to reach the surface accounts for the fact that the formulas do not apply accurately to horizontal surfaces, although in practice the difference is negligible.

Heat Loss by Radiation

The radiation from a window in the wall of a room depends on the temperature of the glass, the temperature of the surroundings, the ratio of the area of the window to the area of the surface towards which the window radiates, the nature of this surface, and upon the wave-length of the radiation. In a house that is nearly free on all sides, the window faces the atmosphere and the ground; if these surroundings act as a black body the loss of heat reaches its largest value, and is given, in calories per square centimetre per second by

$$H = 1.37 \times 10^{-12} e_1 (T_w{}^4 - T_e{}^4) ,$$

where T_w and T_e are measured in ° K.; and in the English system of units by,

$$H = 0.172 \, e_1 \left(\left(\frac{T_w}{100} \right)^4 - \left(\frac{T_e}{100} \right)^4 \right).$$

In these formulas, e_1 is the emissivity of the surface or the emission expressed as a fraction of the amount of energy that the black body would emit at the

same temperature. For the wave-lengths emitted by the warm glass, mainly about 10 microns, glass absorbs quite strongly (1); and its emissivity, e_1, at long wave-lengths is between 0.9 and 1.0.

It is convenient to express the heat that the glass loses from unit area in unit time by the formula

$$H = \frac{5.93}{10^8} \frac{T_w{}^4 - T_e{}^4}{T_w - T_e} (T_w - T_e) e_1 = 5.93 e_1 a(t_w - t_e)$$

the units being Calories per square metre per hour.

If the temperatures remain much below 460° F. (273° C.), the fraction $(T_1{}^4 - T_2{}^4)/(T_1 - T_2)$ depends only on the average temperature $(T_1 + T_2)/2$, since,

$$10^8 a = \frac{T_1{}^4 - T_2{}^4}{T_1 - T_2} = (T_1 + T_2)^3 \left(1 - \frac{2T_1 T_2}{(T_1 + T_2)^2}\right) \doteq 4 \left(\frac{T_1 + T_2}{2}\right)^3.$$

TABLE IV

SURFACE COEFFICIENTS DUE TO RADIATION AT THE AVERAGE TEMPERATURE $\frac{T_1 + T_2}{2}$

°C.	−15	−10	−5	0	5	10	15	20
a	0.69	0.729	0.772	0.816	0.86	0.91	0.96	1.0
$5.93a$	4.09	4.32	4.58	4.84	5.09	5.40	5.69	5.93

°F.	5	14	23	32	41	50	59	68
$0.172a$	0.838	0.885	0.939	1.0	1.043	1.107	1.166	1.215

The coefficients thus calculated may be used to express the heat loss from the surface due to radiation as a function of the temperature difference in the form

$$H = e_1 k_r (t_w - t_e).$$

The Surface Coefficient in Still Air

The contributions that natural convection and radiation make to the surface coefficient at various temperatures are shown in Table V.

Radiation is responsible for about two-thirds and convection for about one-third of the heat loss. Moreover, since for a given temperature of the warm surface, the average temperature and the radiation increase with increasing outside temperature, while the temperature difference and the amount of convection decrease with increasing outside temperature, the two influences are in opposite direc-

TABLE V

SURFACE COEFFICIENTS AS DETERMINED BY RADIATION (UPPER FIGURE) AND CONVECTION (LOWER FIGURE)

t_e, °C.	t_w, °C.			
	0	10	20	30
−20	4.32	4.58		
	2.55	2.84		
−10	4.58	4.84	5.09	
	2.12	2.55	2.84	
0		5.09	5.40	5.69
		2.12	2.55	2.84
10			5.69	5.93
			2.12	2.55
20				6.13
				2.12

tions and in fact practically cancel each other (Table V). The surface co-efficient of a vertical surface becomes a function of the temperature of the warm surface throughout the range of temperatures encountered in the course of the year.

If the coefficients are divided by 4.88, the values to be used with the units B.t.u., ft., ° F. are obtained. For black surfaces ($e_1 = 1$) 100 cm. high, the surface conductances are 1.39, 1.50, and 1.62 B.t.u. per sq. ft. per hr. per ° F. at a wall temperature of 32°, 50°, and 68° F., respectively.

TABLE VI

SURFACE COEFFICIENTS (CALORIES PER SQUARE METRE PER HOUR PER DEGREE DIFFERENCE) AS A FUNCTION OF THE EMISSIVITY e_1

e_1	t_w, ° C.			
	0	10	20	30
1.0	6.79	7.34	7.90	8.42
0.8	5.89	6.37	6.82	7.23
0.6	5.00	5.40	5.74	6.05
0.4	4.10	4.43	4.66	4.87
0		2.84 to 2.12		

The value used in practice has been increased from 1.50 to 1.65 in articles and books dealing with heating and ventilating published in the last few years. It would have been more correct to adopt a co-efficient that depends upon the temperature of the surface. However, since still air conditions usually obtain inside the house, the value of 1.65 is valid where it may be assumed that the surface behaves as a black body in surroundings that may be considered also as black bodies. Walls are not black bodies, and a certain fraction, f, of the radiation is returned, and absorbed by the surface. In the laboratory, windows are tested while forming a cover to a box that is of the same size as the window, cover and bottom being separated by a distance that is smaller than the dimension of the window surface. In this case the heat loss, H, is only the fraction $e_1 e_2/(e_1 + e_2 - e_1 e_2)$ of what it would be with black bodies.

The theory also indicates that the surface coefficient to be used for entire walls is appreciably smaller than the coefficient applying to surfaces not larger than ordinary windowpanes. Under these conditions measurements on an arbitrary vertical surface or window are unlikely to furnish a co-efficient valid in the general case.

Heat Transfer by Forced Convection between a Plane Surface and a Stream of Air

A much larger amount of heat is lost when the wind blows in a direction parallel to the surface of the window. Theory and experiment lead to the formula

$$Q = 0.0356 \, c \, V \, (Re)^{-\frac{1}{2}} \, (t_w - t_e)$$

where Q is the heat lost in Calories per second per metre width,

c is the specific heat per unit volume at constant pressure,

V is the velocity of the wind in metres per second,

Re is Reynolds' number; $\dfrac{\text{velocity} \times \text{length of the plate}}{\text{kinematic viscosity}}$.

When the hour is taken as the unit of time, the formula may be written

$$Q = 5 \, V^{\frac{1}{2}} \, l^{-\frac{1}{2}} \, (t_w - t_a) \ .$$

The length, l, exerts only a slight influence, and in the neighborhood of 1 m. the surface coefficient may be considered as constant. Its value for $l=1$ is given in Table VII.

TABLE VII

SURFACE COEFFICIENT, k_v, OF FORCED CONVECTION

(neglecting the factor $l^{-\frac{1}{2}}$)

Wind velocity, m. per sec.	2	3	4	5	6	7	8	9	10
Q, Cal. per sq. m. per ° C.	8.71	12.4	15.2	18.1	21.0	23.7	26.4	29.0	31.6
Q, B.t.u. per sq. ft. per ° F.	1.78	2.55	3.18	3.72	4.3	4.9	5.4	5.9	6.5
Wind velocity, miles per hr.	4.47	6.71	8.94	11.19	13.42	15.69	17.9	20.1	22.4

The heat loss from the surface is equal to the amount of heat carried away by (i) forced convection as determined by the coefficient k_v, and (ii) the heat given off by radiation and determined by the coefficient k_r at various average temperatures. The old value for the surface coefficient recommended for a wind of 15 miles per hr. is decidedly too low according to the theoretical and laboratory results, since k_v alone is equal to 4.7 B.t.u. per sq. ft. per ° F., and k_r may increase this value to nearly 6 units. This is the value now used in practice and is probably correct for windows, but certainly too large when applied to entire outside walls. Experience also shows that in winds with a speed of 5 m. per sec. or more the flow of the air is no longer steady.

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THE ATMOSPHERIC POTENTIAL GRADIENT
AT OTTAWA, CANADA[1]

BY D. C. ROSE[2]

Abstract

The atmospheric potential gradient was observed continuously at the National Research Laboratories at Ottawa for a year ending December 1, 1935, and at a country station about nine miles northwest of Ottawa, for four months ending November 1, 1936. The country station was set up on a site as free as possible from man-made pollution of the atmosphere. The records were studied from two points of view, the diurnal variation and disturbances in the normal fine weather value of the potential gradient. The results indicate that the diurnal variation is similar to that of other similarly situated stations. The study of disturbances in the potential gradient shows that all disturbances can be correlated with local meteorological conditions. The disturbances were for the most part associated with the stormy conditions usual at the passage of a front. The effect of city pollution on potential gradient records is clearly shown.

Introduction

Measurements of the electric field at the surface of the earth have been generally accepted to indicate that the surface of the earth is charged negatively. A corresponding positive charge exists in the atmosphere, and the small conductivity of the atmosphere allows a continuous positive current to flow to the earth. The maintenance of such a state of equilibrium is thought to be effected by intense reversed currents caused by thunderstorms. Wilson (21) introduced this explanation, and experiments of others (20, 22) tend to confirm his explanation at least in a qualitative way.

The potential gradient under fine weather conditions has a well observed diurnal and seasonal variation which differs somewhat in different localities. Between periods of fine weather with normal undisturbed potential gradient, there are periods in which it is disturbed or deviates in an erratic manner from its normal fine weather value. The object of the present investigation was to stud, the nature of these disturbed periods and their time of occurrence with respec to other meteorological conditions. As the apparatus was made to record the potential gradient continuously, the fine weather variation was also stu 'ied with a view to comparison with other such stations throughout the worl '.

From December 1, 1934, to December 1, 1935, observations were taken at the National Research Laboratories situated on the north side of the city of Ottawa on the bank of the Ottawa River. Here a definite effect was found which would indicate a difference in the behavior of the potential gradient with rising and falling barometer, or with the passage of an anticyclone near the observing station. Owing to the geographic location of the observation point with respect to the city, it was impossible to tell to what extent the deviations from expected potential gradient variations were due to changing electrical properties of the air mass moving across the continent, or due to the effect of pollution from the city carried by winds under different meteorological conditions. Hence, during the late summer and autumn of 1936, a country station was operated at a point about nine miles directly northwest of Ottawa. The site was chosen as far away from inhabited buildings as possible. There was a farmhouse about one-quarter of a mile to the south and two summer cottages about an equal distance to the southeast. Observations were taken during the months from July to October inclusive, and except for domestic cooking in these houses and heating during October, there would probably be no fires. The fires used for cooking would probably be those in small wood-burning or oil stoves, which would usually be burning for only an hour or so before meal times. The village of Old Chelsea is about 1½ miles south of the station, and small settlements of summer cottages are located about a mile to the northeast. There were no industries in any of these localities and it is unlikely that there would be any fires other than those needed for the domestic purposes mentioned above. The railway ran in a NE–SW direction about a mile to the northeast of the station, but it is only a branch line passing through small villages along the Gatineau River; there were only two or three trains a day. Apart from a few small villages scattered along the Gatineau and Ottawa Rivers and a few scattered farms, there are no large residential or industrial areas for some distance, except the cities of Ottawa and Hull and their suburbs. These are centered slightly south of southeast of the station, the nearest outskirts of Hull being about seven miles away. A 50-mile radius would include to the west, south, and east, a few towns of from 2,000 to 4,000 inhabitants, but in northerly directions the country is virtually uninhabited except for small scattered villages and farm areas along the Gatineau River and more distant lumber and mining centres in Northern Ontario and Quebec. Hence, except for the effect of the proximity of Ottawa and Hull, the air at the country station is about as free from artificial pollution as any that could be found without moving unreasonably great distances from civilization. In regard to pollution from Ottawa and Hull, the wind seldom blows from the southeast direction for any length of time, so the country station is about as well situated with respect to these cities as it could be.

The situation at the laboratories in Ottawa is such that to the north and west, except for the small village of Gatineau Point, there is no large residential or industrial area for great distances. In fact, from a line northeast from

the laboratories to a line west from the laboratories, there should lie no source of pollution of any magnitude except the laboratory heating plant (the chimney of which is about 100 yd. north from the collecting electrode) and a cement works about $1\frac{1}{2}$ miles WNW. The laboratory heating plant appeared to cause no trouble except on rare occasions when the smoke hung around the corner of the building where the electrode was situated. The plant is built on the side of a cliff below the laboratories and the elevation of the top of the chimney is about 15 to 20 ft. below the level of the collecting electrode. In fine weather the wind and eddy currents are such that the smoke is blown well away from the building before rising to the height of the electrode. Only on a few occasions throughout the year was any movement of smoke towards the electrode noted.

Apparatus

The schematic diagram of the arrangement of the laboratory recorder is shown in Fig. 1. The window through which the collector projected was about 30 ft. above the ground on the northeast end of the laboratory. The
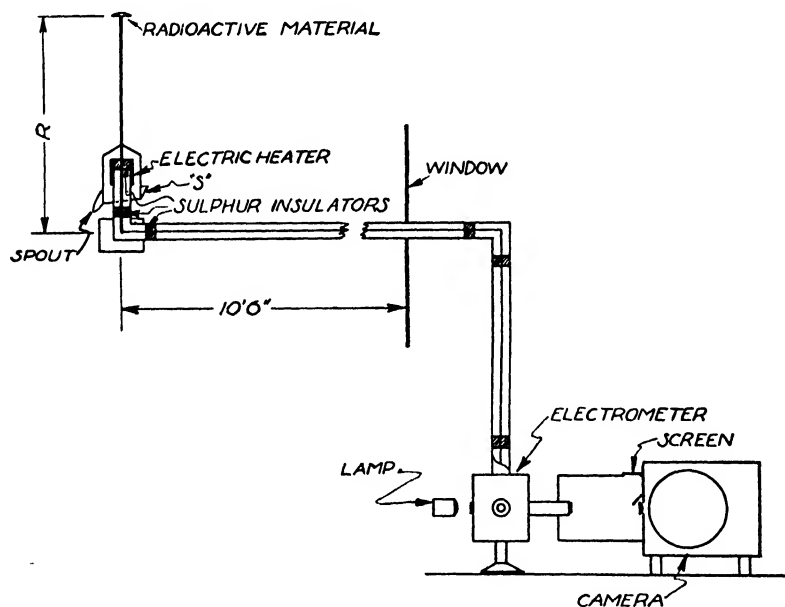
Fig. 1. *Diagram of apparatus at the laboratory station.*

insulation used was sulphur. The design of the weatherproof head supporting the radioactive collector system proved to be very satisfactory once the electric heater was installed. This heater consisted of a few turns of nichrome wire wound on asbestos paper around the vertical tube holding the supporting insulators. The temperature was kept a few degrees above the surrounding air temperature. The inverted skirt, S, surrounding the bottom of the weather shield, was an important feature in collecting rain·and draining

it off through the spout in such a way that the water cleared the grounded parts. The insulation in this apparatus could be maintained in good condition through many hours of steady rain, provided that winds were not high enough to blow moisture up under the shield covering the insulators. The distance from the window to the collector was 10 ft. 6 in., and two different heights, R, were used for the collector, namely 31 and 21 in. A simpler design of collector support and insulated system not extending so far out from the window would have been equally satisfactory. This apparatus was designed primarily to support a sphere for observing potential changes when there were lightning flashes. For such observations, it was desirable to have it extend out as far as possible from the wall of the building. It proved, however, a satisfactory potential gradient recorder, except for the fact that the whole apparatus had to be withdrawn into the room to make a proper test of the insulation. This did not have to be done oftener than about once a month, because experience showed that apart from some trouble with insects in the autumn of the year and except for rare periods of exceptionally severe weather conditions, the insulation remained good almost indefinitely, and during bad weather it was either quite good or so definitely bad that there was no doubt about its behavior. Some trouble was experienced, particularly at high potential, with the accumulation of charges on the sulphur. This would have the effect of an apparent leak, when the potential was changed suddenly, which would practically disappear in a few minutes. This would introduce an error in rapidly changing potential gradients, but as under such circumstances the value could not be measured with any great accuracy this effect was not considered important. The radioactive collector was of sufficient strength that the insulated system would acquire half its final potential in less than 30 sec., and the insulation leak was always sufficiently high compared to this to cause negligible errors of registration except under extreme weather conditions. When there was any doubt at all about the insulation, the records for such periods were omitted from the analyses of the results.

A rotating drum camera in conjunction with a single-fibre electrometer was used for recording. The camera was driven by a weight, the rate being controlled by a telechron motor in such a way that it rotated once in about 26 hr. The record was changed every 24 hr. The 24-hr. record was about 29 in. long, so that one inch represented a little less than one hour. A commutator arrangement (not shown) grounded the electrometer and applied fixed positive and then negative voltages to the insulated system for a few minutes every four hours. These points were used for time reference points on the record, and the impressed voltages gave an indication of the accuracy with which the electrometer retained its calibration. The potential gradient could be observed at any time, as a mirror situated just above the cylindrical lens, which focused the fibre on the photographic paper, reflected a part of the image of the fibre on a horizontal ground glass screen and scale in the housing of the camera. The distance of this scale from the microscope was the same as that of the photographic paper, so a calibration on this scale

required no further interpretation to convert measurements, on the record, to volts. The electrometer retained its calibration with sufficient accuracy that a careful calibration about once a month was sufficient. The photographic record was three inches wide. The zero position was adjusted slightly off centre so that actual voltages from 325 positive to 250 negative could be recorded.

The same recording apparatus was used at the country station. The collector system is somewhat different and is shown in Fig. 2. The apparatus was housed in a box 6 by 3 by 3 ft., the long dimension being horizontal. The box was mounted on a frame about 3 ft. off the ground. A turret, 1 ft. square, rising vertically 3 ft. at one end of the box, supported the collector and weather proof insulated system. The collector was 9 ft. 8 in. in height from the ground. The design of the insulated system was somewhat different from that used in the laboratory. Sufficient details are given in the figure that no further description should be required here.
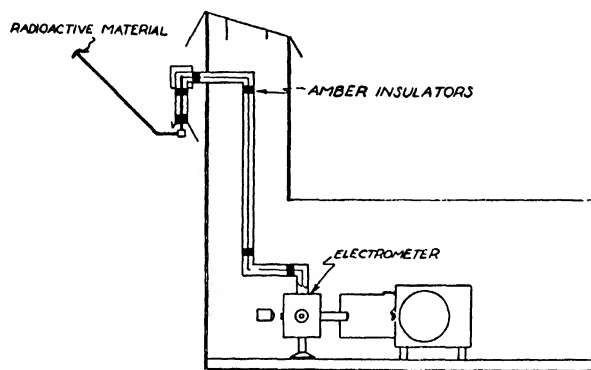
FIG. 2. *Diagram of apparatus at the country station.*

A radioactive collector similar to the one used with the laboratory recorder was employed. The insulation in this apparatus was amber throughout and it proved much more satisfactory than sulphur. Its insulating properties appeared to be better and no accumulation of charge in the insulators was noted. Tests were made regularly and the insulators, when charged to about 150 volts with the collector removed, showed no measurable loss of charge in periods of two minutes or so. Rain flurries did not affect the insulation, though it would usually break down after two or three hours of steady rain. It was noted that the process of loss of insulation due to moisture on the surface of the outer insulator took place and cleared in relatively short periods of time. With continued heavy rain, the insulation would remain quite good for some time, then would break down to a very low value (so low that no potential would be recorded) in the comparatively short period of half an hour to an hour. The time from effective short circuit of the insulated system to good insulation would be of the order of an hour after the rain stopped and the air became dryer. The amount of rain the system would

stand and the time required to recover after loss of insulation depended on how often it had been subjected to such conditions since last being overhauled. Complete overhaul was required only three times in the four-month period during which the station was operated. This was done by dismantling all the insulators except those in the electrometer and turning a layer off the exposed surfaces.

The camera was driven at about half its previous speed; the record was therefore changed every 48 hr. instead of every 24 hr. Between replacements of the photographic paper the apparatus ran with no attention. The time required to renew the photographic paper, test the insulation, etc., was from one-half to three-quarters of an hour. As no electric power was available at the country station an ordinary alarm clock was adapted to control the speed of the camera, and current for the illuminating lamp was supplied from a storage battery which could be used for four days without recharging.

The radioactive collector used in both the laboratory and country stations was made from old glass radon seeds, the glass being broken up and stuck on a copper plate with a layer of shellac thin enough to allow the passage of α-particles of reasonable range. A copper plate was mounted on the under surface of an inverted saucer-shaped disc of dural. This disc was supported by a 1/4 in. dural rod as shown in Figs. 1 and 2. This collector (Ra D, E, and F mixture in equilibrium) has the advantage that it is easy to obtain and its decay period is long, but the disadvantage is that it emits weak β- and γ-rays, as well as α-rays. The effect of γ-rays in causing an insulation leak in the electrometer was shown to be too small to be considered. The effect of β- and γ-rays on increasing the rate of ionization in the neighborhood of the collector would result only in a lowering of the effective height of the collector. This would cause the potential gradient readings to be low by a constant factor. Without definite knowledge of the quantity of the radioactive material on the collector, it is difficult to estimate the possible magnitude of the effect. A rough examination of radioactive data shows that the γ-rays would contribute very little once a distance of several centimetres from the collectors was reached, but β-rays would be relatively more effective in creating a general increase in ionization at a distance of a metre or two from the collector. The error would certainly not be large in the present case, as the magnitude of potentials found agrees well with other stations similarly located.

In the present investigation, variations in the potential gradient rather than ts absolute value were being studied; hence no serious attempt was made to obtain a very accurate reduction factor. The reduction factor necessary to correct readings at the laboratory station to volts per metre was measured approximately by means of a portable electrometer and a wire stretched over the ice on the Ottawa River behind the laboratory. This was the largest flat area free from trees near the laboratory building. At the point where the observations were taken the river is about 1/4 mile wide and the building is situated about 100 yd. from the bank of the river.

The height of the window above the water level is approximately 75 ft. The horizontal wire was stretched about one metre above ground and was about 50 ft. long between insulated supports. A radioactive collector, probably a little stronger than that used on the registering apparatus, was placed at its centre. Observations were taken on two days for about an hour and a half about noon of each day. On the first day the potential gradient was in a disturbed state, and, while the general nature of the variations observed on the river and those recorded in the laboratory were the same, there was considerable difference in detail. For instance, a reversal in the potentials observed on the river showed up only as a reduction to about half its normal value at the laboratory. On the second day, except for a short disturbance which showed the opposite effect, that is, a reversal in the laboratory which did not appear on the potential observed on the river, the curves were parallel for an hour and a reduction factor could be estimated. The factor so found was 0.77. In view of the fact that the factor is estimated from observations extending over a single hour on one day, and in view of the difficulty in knowing the exact effective height of the collector, no great accuracy is claimed for the reduction factor. According to Scrase (16) the most reliable exposure factor is obtained by means of a test plate placed in the roof of an underground laboratory. Such a method could obviously be used only in an observatory containing such equipment. Unfortunately this reduction factor was applicable only to the results taken between December 1, 1934, and April 13, 1935, since on the latter day the rod, R, (Fig. 1), supporting the collector was reduced in length in order that the sensitivity of the electrometer could be increased somewhat to improve the focus of the fibre at the extreme ends of the scale. To compare the results before and after this change, a factor (apart from electrometer sensitivity corrections) was used which was merely the inverse ratio of the lengths of the insulated rod from the centre of the head (Fig. 1) to the collector. There is no justification for the procedure except that the annual variation curve (Fig. 3) shows no greater discontinuity between April and May than between some of the other consecutive months. There was a disturbance during virtually all the latter half of April, so the value for April was obtained practically entirely from observations made during the two weeks before the change was made. No attempt was made to obtain a reduction factor for the country station.

In reading the records, the zero line was drawn by joining the points on the record where the electrometer was grounded. Hour marks were indicated and the deflection was measured by scaling with a steel scale divided in half millimetres. Measurement could be made to 2 or 3% when the potential gradient was steady, but under ordinary daytime conditions small rapid variations usually occur, which make it difficult to measure the exact value from the record to better than from 5 to 10%, depending on the magnitude of the deflection at the hour concerned. With this in view, to save time in measurement, readings were taken to the nearest half millimetre deflection of the electrometer. Instead of obtaining a true average by estimating

the average of the potential for an hour centered about the time for which the reading is tabled, the value used for each hour was the actual value at that hour. This method was adopted as it appeared more suitable for the study of potential gradient disturbances discussed in the latter parts of this paper. Where fluctuations were so great in magnitude and rapidity that a spot reading could not be obtained, the mean over a period of from five to ten minutes before and after the hour was estimated and entered as the value at that hour. The time marks and the setting of the clock were kept with such accuracy that the probable error in location of hour marks would never be greater than two or three minutes difference from Eastern Standard or 75th meridian time.

Results

DIURNAL VARIATION

Fig. 3 shows the diurnal variation means for each month, except August, at the laboratory station. The author was absent for the greater part of August and the apparatus was not operated. Fig. 4 shows similar curves plotted to a larger scale for the four months in 1936 during which the country station was operated, the mean for the four months, and the mean for the year at the laboratory station. Owing to the fact that the reduction factor was known only approximately, these results are plotted as per-

FIG. 3. *Annual and diurnal variation at the laboratory station.*

centages of the mean rather than in volts per metre. The mean value of the potential gradient for the year at the laboratory station, using the approximate reduction factor discussed above, was found to be 118 volts per metre. These curves represent observations taken during fine weather conditions only. In the case of the country station the curves include practically all observations, except those taken during obviously disturbed or stormy

conditions. In the case of the laboratory station, a different criterion was used. The hourly readings were taken for every hour at which a reading could be obtained, that is, omitting only hours when the insulation was bad, the potential was so high that the fibre was off the scale, or the fluctuations so great and so rapid that no reading could be obtained. These were averaged for periods of half a month, and a smooth curve drawn through the points was thus obtained. The differences between the individual hourly observations and points picked from the smoothed curve were plotted. Such a curve is shown in Fig. 5. The differences were plotted without respect to sign for the sake of convenience. When these differences were less than 150 volts (not corrected by reduction factor) for a period of four hours or more, the readings were taken as representing undisturbed conditions. This practically limits readings to periods of rising barometer and winds in the north to
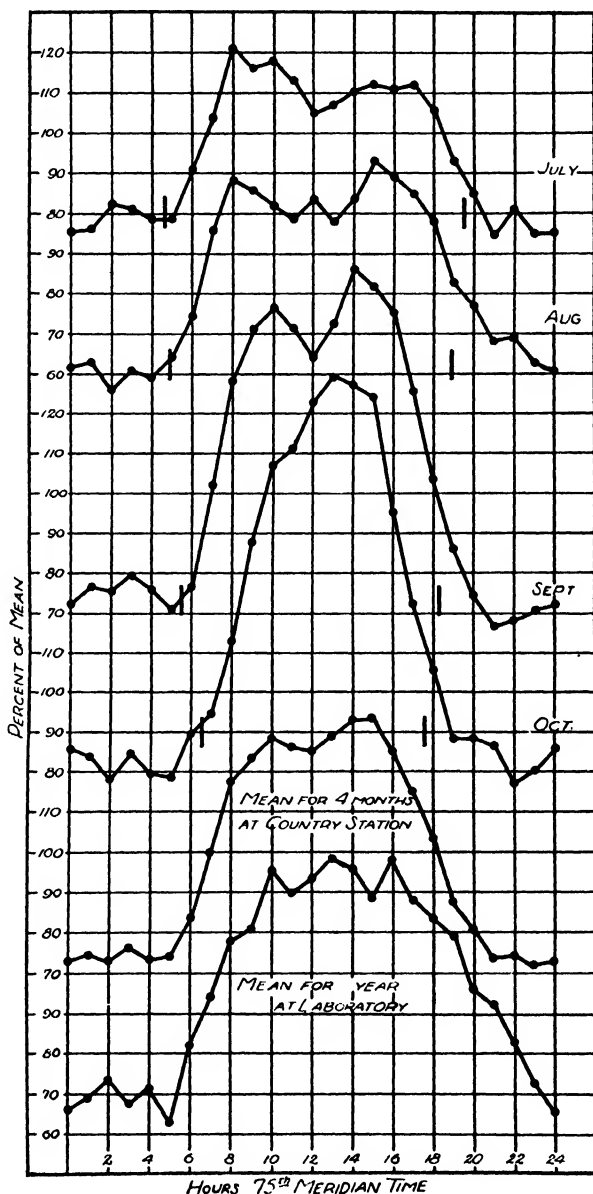
FIG. 4. *Diurnal variation at the country station, and mean for year at the laboratory station*

west quadrant.   The reason for this is discussed in a later section on potential gradient disturbances.

The diurnal variation is in general agreement with most similarly situated stations at various places throughout the world.   The diurnal variation of the potential gradient over land usually contains an early morning minimum, a morning maximum, a daytime minimum, and an evening maximum.   This variation is considered to be made up of local effects superimposed on the well known world time variation which is observed at sea.   As shown by Mauchly (12) the mean diurnal variation curve at sea has a total variation of the order of 30% of its mean value, and a single maximum at approximately 14 hr. 75th meridian time.   Hence, in the curves shown in Fig. 4 the daytime minimum is less pronounced and the afternoon maximum is somewhat enhanced by the effect of the universal time variation.   The results at the country station show that this enhancement is more noticeable in September and October where the universal time maximum and the afternoon maximum more nearly coincide than in July and August.   The monthly mean curves shown in Fig. 3 were too erratic to justify plotting on the large scale used in Fig. 4, and the effects of the universal time variation and the definite morning and afternoon maxima are correspondingly less pronounced.   This is not unexpected when the total times during which the potential gradient could be considered undisturbed are compared at the two stations.   Table I, Columns 2 and 5, shows the number of hours each month for which the potential gradient could be considered to be undisturbed.   Columns 3 and 6 show this same number in percentage of the total number of hours the station was operated.   The difference in the values at the laboratory station and at the country station are apparent.

TABLE I

HOURS OF UNDISTURBED POTENTIAL GRADIENT

Month	No. of hourly observations	% of hours station was operated	Month	No. of hourly observations	% of hours station was operated	Monthly mean volts
1934 *Laboratory station*			1935 *Laboratory station*			
Dec.	128	22	Sept.	184	26	
			Oct.	191	28	
1935			Nov.	176	25	
Jan.	181	26	1936 *Country station*			
Feb.	133	20				
Mar.	141	19				
Apr.	113	17	**July	691	85	120.7
May	199	31	Aug.	538	72	107.6
June	160	23	Sept.	461	68	136.3
*July	79	19	***Oct.	435	54	143.2
Aug.	—	—				

*July 1 to 20 only.   **June 26 to July 31.   ***Oct. 1 to Nov. 3.

It is generally considered that the potential gradient at the earth's surface is caused by the fact that the potential of the high conducting layers in the atmosphere is raised above that of the earth either by charges carried upwards during thunderstorms or by some unknown means. The fact that the air is continuously being ionized by radioactive matter in the air, cosmic rays, etc., means that a space charge is set up. The properties of the ions producing the conductivity and magnitude of the effects involved are such that the space charge is mainly concentrated near the surface of the earth, the potential gradient decreases, space charge decreases, and conductivity increases rapidly with height above the earth's surface (2, 3, 7). Hence, at the earth's surface, the potential gradient would be expected to depend to a great extent on local conditions which affect the ionization equilibrium. For the present the effect of rain, charged clouds, etc., which represent disturbed conditions, will be omitted, and will be discussed in the next section of this paper.

The fundamental variables which control the potential gradient are considered to be: i, the air-earth current; λ, the conductivity; F the potential gradient, the equation $F = \frac{i}{\lambda}$ being supposed to hold at the surface of the earth. If one accepts the Wilson theory that the atmospheric electric phenomena are due to the transport of charges by thunderstorms to high conducting layers in the atmosphere, then the potential gradient would be expected to depend on this phenomenon. On the other hand it is well known that the conductivity depends on the rate of production of ions, q, the number of condensation nuclei, Z, and the conditions of equilibrium between production and loss of small ions, formation of large ions, etc. In localities where the number of condensation nuclei is relatively unimportant, such as at sea, and in polar regions, the universal time variation in potential gradient has been shown by Whipple (19) to agree with an estimation of the time variation in thunderstorms throughout the world. Whether this is a sufficient explanation of the universal time variation in F would depend on the nature of variations in the rate of ionization, q, at the surface of the earth. This is a difficult quantity to measure directly, but some experiments indicate that it cannot be treated as constant. Nolan and Nolan (13, 14), from indirect calculation of q, show that its diurnal variation resembles that of the potential gradient, and Hogg (9, 10) has indicated the possibility of a universal time variation of the rate of ionization which is in phase with that found for the potential at sea. Hence, we have two possible and independent explanations of the universal time variation in potential gradient.

The effect of condensation nuclei on the potential gradient is due to the effect of nuclei on the conductivity. The equilibrium relations between small and large ions, nuclei, etc., have been discussed by many investigators. In thickly populated areas and to a lesser extent in rural areas, the effect of nuclei is far more pronounced than the effect of variations in the rate of production of ions or in the air-earth current. Qualitatively the effect of nuclei is described by Scrase (16). The explanation of the double peak in the

diurnal variation curve found at Kew was advanced by Simpson, and is as follows: Smoke (from domestic and industrial sources) increases from about 5 hours until 9 hours, and, as convection during this period is small, pollution increases rapidly; this results in an increasing potential gradient. During the day, convection is greater and the air near the ground is cleared at the expense of the air higher up. During the evening the reverse is true and a second maximum appears.

In Fig. 4 the approximate times of sunrise and sunset are marked for the middle of each month, and it is noted that the potential gradient starts to increase immediately after sunrise. The afternoon maximum for September and October is more prominent than the morning maximum, though in the case of July, August, and the mean for the year it is of approximately the same magnitude. A longer series of observations would, of course, be necessary to decide whether or not this has any real significance. If a true separation of the universal time variation and the local variation could be made, the afternoon maximum would probably be less than the morning. If the approximate method given by Brown (4) to make such a separation is used this appears to be the case. Brown also collected results from several places throughout the world and these show considerable differences in the relative heights of the morning and afternoon maxima. For instance, Allen (1) found virtually no afternoon maximum at Mount Stromlo, while at other places it is equal in prominence to the morning maximum. The above explanation of the reason for the diurnal variation does not explain these differences.

That separate effects due to artificial and natural pollution are apparent is shown by an examination of stations like Kew. That the effect here is mostly due to artificial contamination is apparent from the fact that the position of the morning maximum varies less with the seasons than at many other places, and it moved forward an hour at the advent of daylight saving time (16). The observations at the country station described here show such a consistent variation with the time of sunrise that the effect would seem to be entirely natural. The same variation with sunrise is shown by Allen (1) at Mount Stromlo, but only to a lesser extent at Hotel Canberra. In the case of Johannesburg, Halliday (8) shows a variation in time of morning maximum which tends to follow the time of sunrise during the months from April to November, and then some other influence becomes prominent which makes the morning maximum late and the evening maximum irregular. The explanation of these differences, no doubt, lies in differences in pollution due to different situations with respect to sources of pollution and to local meteorological conditions.

Wait (18) made a series of observations for a short period in 1929 at a station remote from any industrial centre at Penalosa, Kansas, about the geographical centre of the United States. The results indicate a curve fitting very closely in phase and relative magnitude to the diurnal variation found over oceans when plotted in universal, rather than local, time. In the present experiment

at the country station northwest of Ottawa, though different results were obtained, it would be expected that the amount of man-made pollution would be almost as small as at Penalosa.   The same probably applies to the several other stations such as Mount Stromlo, if one can take the regular movement of the position of the morning maximum with the time of sunrise as an indication of lack of man-made pollution.

Brown has classified stations according to latitude, and observes corresponding differences based on the shape of the curve after separating the universal time variation.   That a classification according to latitude is natural is seen when one considers the variation in time of the morning maximum.   If it follows sunrise at all stations, the result will be a different diurnal variation at different latitudes when averaged over a year.   He also finds two types at mean latitudes, a broad type and a narrow type. In the case of five out of the six stations showing the broad type he points out that the station was probably situated in locations subject to considerable man-made pollution.

In conclusion, it may be stated that the results of the present observations agree in general with others.   Detailed comparisons as outlined in the above paragraphs with other stations show differences which will probably require simultaneous observations of complete local meteorological conditions as well as other atmospheric electrical quantities at several stations for a complete explanation.

ANNUAL VARIATION

Owing to the uncertain value of the reduction factor, the annual variation curve shown in Fig. 3 (laboratory station) has no great significance except that it shows that the annual variation is not great.   The curves show voltages and are not reduced to volts per metre (see paragraph on reduction factor). The general shape of annual variation curves at other stations shows a higher value in winter than in summer (8, 16).   This would be expected to be particularly prominent at stations like Kew, where the influence of fires for domestic heating is felt.   In the present case, owing to the location of the laboratory with respect to the city and the criterion used to select records to be included in the curve, the effect of city pollution should be small.   The deviations from the mean value for the laboratory station when compared with those for the country station show that the effect of city pollution was not entirely eliminated, but the effect of increased use of fires for heating during the winter would be expected to be compensated somewhat by the blanket of snow which covers the ground from about mid-December until mid-March. A certain number of the nuclei which affect the gradient must come from the ground.   When the ground is covered with snow, virtually none of these would be stirred up, and the snow blanket would act as an absorber of any nuclei which settled on it.   The means for the four months during which the country station was operated are shown in the last column of Table I. They show a tendency to increase towards winter but the station was closed before any snow fell.   It is unfortunate that work at the country station

could not be carried on through the winter to obtain more information on the effect of a snow blanket on the diurnal curves in Fig. 4, as well as on the annual variation.

POTENTIAL GRADIENT AND AIR MASS ANALYSIS

Little can be said from these observations about differences in the fine weather value of the potential gradient and different types of air mass. The air mass at Ottawa is usually Polar Continental or Transitional Polar Continental, the dividing line between these being not very definite, particularly in summer. Occasionally there is an inflow of different air from more tropical regions, or a recession of a mass of polar air which has moved down from the northwest and then moves back from a southwesterly direction. Southwest winds also occur which are usually associated with the passage of a barometric depression, but under such circumstances stormy conditions usually prevail and the potential gradient is disturbed owing to rain, excessive turbulence, etc.

Lansberg (11) found differences in the nuclear content with different air masses, and corresponding differences in the potential gradient would be expected. This is particularly true in view of the great differences in moisture content of polar and tropical air masses. The increased moisture content of air masses which have remained over such areas as the Great Lakes for some time would also be expected to affect the potential gradient. An examination of weather maps showed only four or five cases of a definite movement of an air mass from the south or southwest in the four months during which the country station was operated; that is, apart from periods when a definite weather disturbance was passing. One such case is described in detail in the next section, September 22 to 26, Fig. 7. An examination of this case showed that the potential gradient on September 22 and 23 was, for the most part, higher than the mean for the month. The same applies to one other day on which there was air movement from the southwest. On one day the potential gradient was definitely low during southwest winds, and other periods show no consistent difference. The small number of data here are not considered to be sufficient to give definite information on this point.

DISTURBANCES IN THE POTENTIAL GRADIENT

It is well known that stormy weather has an important influence on the potential gradient. Dust storms are reported to cause high negative potentials and its effect on potentials during thunderstorms has been definitely shown. Rain is also known to be charged, and, hence, has an effect on the potential gradient. On the other hand, clouds, except cumulus clouds under certain conditions, appear to have no appreciable effect on the potential gradient.

As stormy weather conditions in the climates at this latitude are usually associated with instability created at the "front" separating air masses of different properties, it would be expected that atmospheric electric phenomena would be considerably disturbed at the passage of a front over the station, or

while being influenced by an overhead frontal surface due to overrunning air. The potential gradient observations taken at the laboratory and at the country station were examined with a view to studying the relations between the potential gradient disturbances and the passage of fronts. For the six months of the year the laboratory station was operated, and for the four months that the country station was operated, weather maps* were obtained showing the frontal systems over Canada and the United States. The comparison of the potential gradient records with the weather maps shows that disturbances always occur at the passage of a front, and, in fact, practically all disturbances in the potential gradient where observations were completed can be explained by local meteorological conditions.

The effect of the front in producing a potential gradient disturbance is best shown by plotting deviations from the mean diurnal variation. To do this the hourly means, including all hours when a reading was obtained, covering periods of half a month were plotted. A smooth curve** was drawn through the points, and the hourly values so found were subtracted from the individual hourly readings. The differences were plotted on a time scale and placed parallel to the barograph record for comparison. The differences were plotted without respect to sign for the sake of convenience. In using hourly rather than a shorter interval between readings, disturbances of less than an hour in length would be missed if they occurred between readings. In disturbed periods, oscillations of the potential gradient over a wide range may take place in a few minutes, but as the disturbed period virtually always lasts several hours and the detailed shape of the disturbance was not being studied, hourly readings seemed quite satisfactory to show the required effect. In fine weather, isolated disturbances of less than an hour's duration rarely occur.

Before examining the figures showing samples of the disturbance found at the passage of fronts, consider what would be expected from general knowledge of potential gradient behavior discussed previously. First, the amount of disturbance in the potential gradient would be expected to bear some relation to the amount of instability in the air at the passage of the front. This will depend on the strength of the front and how near a wave in the front containing a low is to the point of observation. In an idealized system like that shown in textbooks on meteorology (5) in which a warm front is followed shortly by a cold front, one would expect no disturbance in the potential gradient until the nimbus clouds at the warm front passed overhead. The potential gradient would become normal again when the warm sector was overhead and again be disturbed when the cold front passed over. In fact one would expect only disturbances due to rain and increased turbulence at the passage of the fronts, perhaps complicated by the electrical disturbance

*These maps were borrowed from the Dominion Meteorological Office, Toronto. The author wishes to thank the Director, Mr. J. Patterson, for his assistance in giving meteorological information.

**In the case of the country station the points fitted a smooth curve sufficiently closely that they were used rather than the smooth curve.

produced by an occasional thunderstorm. If the normal balance between ionization and nuclear content were different in the different air masses, of course a different steady value for the potential gradient would be expected while the warm sector was overhead. Actually fronts do not often appear in this ideal manner but are usually much more complicated. Often several fronts of different types and of greater or less strength pass over the point of observation in a few hours.

To separate the effects of rain, thunderstorm, and generally increased mixing by turbulence would require much more detailed meteorological observations than were taken. The work of Nolan and Nolan (13, 14) would indicate that the effect of rain would be complicated, depending largely on the relative numbers of drops of different sizes. On the average, small drops were found by Nolan and Nolan to carry negative charge and large drops positive, but the space charge set up thereby is complicated by the relative rates of fall of drops of different sizes. Added to this there is the fact that charged rain actually puts charges on the exposed collector, and also the possibility of charges being generated by the breaking up of water drops striking the collector. Of course as the water drops off, a charge is carried away but not necessarily of the same magnitude as that given to the collector by the incident rain. To try to estimate the effect that charges carried to the collector by rain would have on potential gradient readings the following rough calculation was made. On the assumption that the action of the radioactive collector could be treated as a resistance connecting the collector to an equipotential surface at the potential the collector would reach under ideal conditions, a calculation of the value of the resistance can be made from the capacity of the insulated system, and the time it takes the potential to reach say within $\frac{1}{e}$ of its final value after the collector is grounded. The capacity, though not measured, is estimated at 50 $\mu\mu$f., and the time for the potential to reach within $\frac{1}{e}$ of its final value was less than one minute with the collector used. This would indicate a resistance of 1.2×10^{12} ohms or less. Now, the current flowing to the electrode because of rain may be calculated for a hypothetical case where all the rain was retained in the collector and supporting rod, so that all charge acquired from the rain would be retained. On the assumption of a rainfall of 0.5 mm. per hr. and a charge of 0.5 e.s.u. per gm.* the current flowing to a collector of projected area of 60 sq. cm. would be 1.4×10^{-13} amp. Obviously the collector used would cope with this amount of rain without any great error in potential reading. On the other hand, the effect of rain in splashing against the collector and producing charges by the Lenard effect may create considerable error in potential gradients, particularly in heavy rain. Nolan and Nolan (13, 14) in studying ionization and nuclear content find evidence of such an effect, so this should be included among the complications involved in discussing the measurement of potential gradient during rain. According to the Lenard effect the breaking up of rain drops in air causes the formation of negative ions, the drops retaining a

Smithsonian Physical Tables, Eighth Revised Edition, page 598.

positive charge. Nolan and Nolan also found a large increase in negative ionization during heavy rain which may be due to splashing. No attempt was made to investigate this effect in the present case, though it might be expected to show excessive positive gradients.

The effect of thunderstorms near the apparatus is of course well known. The potentials during thunderstorms are so high and variable that when such a storm was near, either the fibre would be off the scale or fluctuating too rapidly to leave a measurable photographic record.

Occasionally a front may pass the station carrying no nearby depression wave and without precipitation. In such a case the change in wind direction and velocity would be expected to have an effect on the potential gradient.

Besides the above-mentioned effects, continued rain for several hours destroyed the insulation. Hence, detailed observations throughout the passage of the front were not always obtainable. The results obtained indicate, however, that there is no characteristic behavior of the potential gradient at the passage of a front. Sometimes it stayed off the positive end of the scale for a few hours, sometimes off the negative end, and it often oscillated irregularly over a range from several hundred volts above its normal value to several hundred volts below. In view of the failure of the insulation during extreme weather conditions, it did not seem worth while to make a detailed statistical study of the magnitudes or times of positive and negative deviations from normal values during disturbed periods. For this reason as well as for greater convenience, the deviations from the mean are plotted without respect to sign.

Barograph records were taken and for part of the time at both stations a recording thermometer was operated. Weather notes were taken usually twice each day, at about 9 hours and 17 hours. As only part of the author's time was available for this investigation these are not as detailed as might have been desired. Further, notes taken in Ottawa would not be applicable in detail to the country station, particularly in regard to times of rainfall. In circumstances characterized by local thunderstorms or rain flurries often just after the passage of a cold front (such as instability in the new air mass or overrunning air from the warmer air mass), storms appear to occur at the country station much oftener than, and not necessarily at the same time as, at Ottawa. In fact from casual observation it seems likely that the average rainfall at the country station would be considerably higher than in Ottawa, though the station is only about eight miles away and of about 300 ft. higher altitude. No definite rainfall data were obtained on this point.

From a study of the daily weather maps published by the Dominion Meteorological Office, other maps showing movements of fronts, and the weather notes taken, practically every potential gradient disturbance at the country station can be explained by local weather conditions. At the laboratory station the same appears to be true but the effect of pollution from the city is added.

DESCRIPTION OF FIGURES SHOWING THE POTENTIAL GRADIENT DISTURBANCES AT THE PASSAGE OF A FRONT

In Figs. 5 to 11 the deviation from the means are plotted in actual volts observed, no reduction factor having been used.   When the disturbance was such that the image of the electrometer fibre was off the scale or moving over large voltage ranges so rapidly that no photographic trace was obtainable, the difference is shown as being off the scale on the figure, *i.e.*, higher than 300 volts.   Where such a condition existed for several hours, short lines at the top of the graph are shown to indicate that the reading was off the scale continuously.   The ordinate may be taken as representing the magnitude of the disturbance in the potential gradient.   The barometer record is plotted above the potential deviation and weather maps below showing the approximate position of fronts at 8 a.m. on the days concerned.   Only the region including the Great Lakes up to James Bay and the eastern states is included. Ottawa is shown by the black spot slightly right of centre.   Centres of low and high pressure are marked *L* and *H*, and in some cases when they occurred just off the area covered by the map they are shown in a circle with an arrowhead pointing in the direction in which they are located.   No distinction is made on the map between cold and warm fronts as there appeared to be no difference in the effect on the potential gradient, except perhaps in the time and duration of disturbance due to the different slope of the frontal surface. The usual motion of air masses in this district is a series of anticyclones moving in from the northwest or west, and if a depression in a front moves in such a way that a warm front passes Ottawa it is usually followed rapidly by a cold front.   As there is an infinite variation in strength, shape, rate of motion, etc., of fronts and potential gradient disturbances are correspondingly different, it is difficult to generalize; hence, several examples are shown below and each described briefly.

Fig. 5, July 21 to 24, 1936, Country Station

The potential gradient deviation on the first two days is typical, in the undisturbed state, of anticyclonic fine weather conditions.   On the morning of the 21st the sky was clear except for some cirrus clouds; there was a slight haze and light northerly winds.   During the afternoon alto-stratus clouds were forming.   On July 22 the sky was partly overcast with alto-stratus and cumulus clouds; there was no wind in the morning but there was a light southwest wind in the afternoon.   A small potential gradient disturbance occurred during the morning.   This is perhaps due to a change in wind direction, or to a rising wind.   Such a weak disturbance in the potential gradient is sometimes noted as an anticyclone centre passes over involving a change in wind direction.   A system of two fronts, the first being quite weak, was approaching from the west.   The first front passed during the morning of the 23rd but the potential gradient disturbance started much earlier.   Rain fell early in the morning, perhaps starting at the time of the first disturbance in the potential gradient.   The weather did not clear to any extent until after the passage of the second front early on the 24th, though for a time on the 23rd

the overcast sky tended to clear and rain fell only for short periods.   On the morning of the 24th the sky was completely overcast with nimbus clouds. The rain stopped during the morning.   The wind shifted to NNW, the barometer started to rise, and the sky began to clear—typical of the passage of a cold front.   The potential gradient disturbance cleared shortly after the passage of the front as shown in the figure.
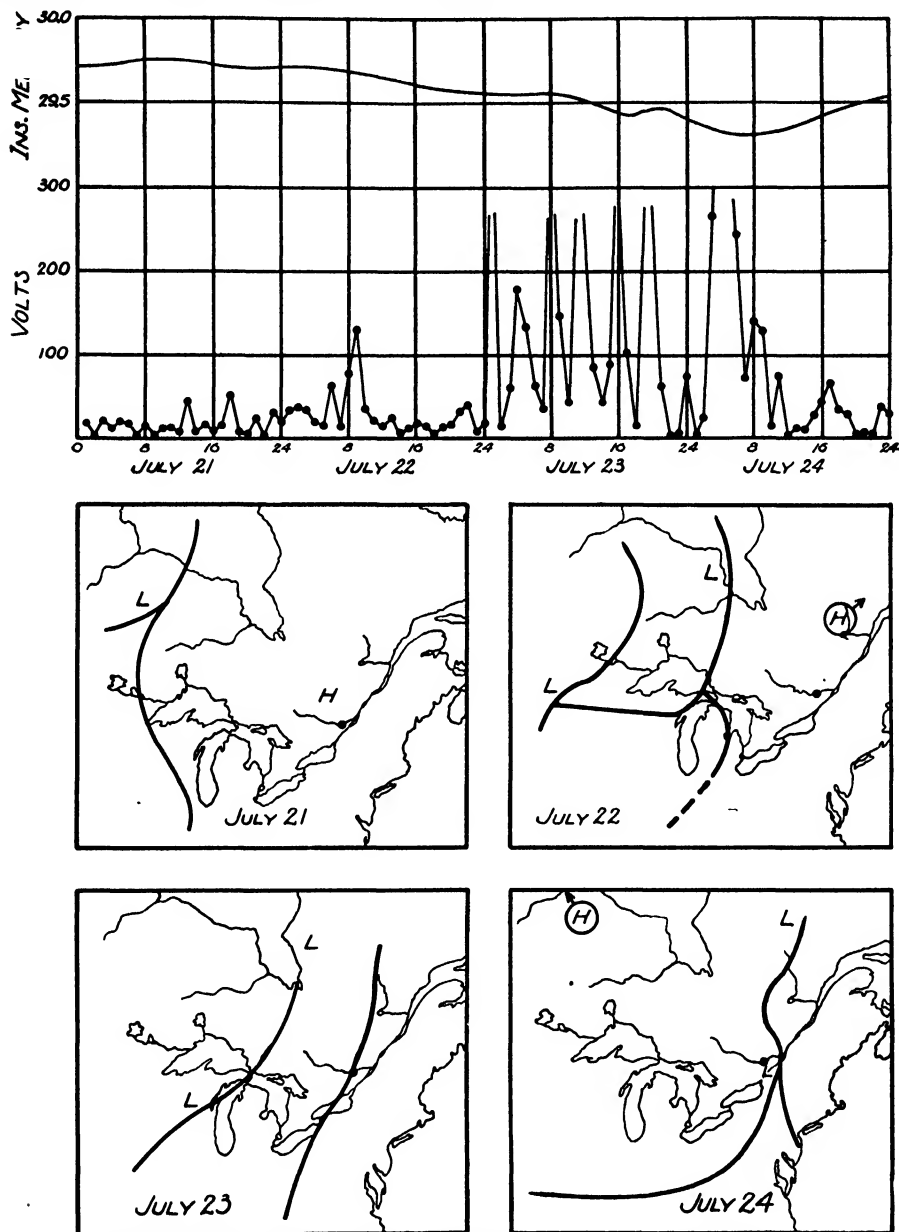
FIG. 5.   *Potential gradient disturbances and weather map, July 21-24, 1936, country station.*

Fig. 6, August 9 to 11, 1936, Country Station

This is an example of the passage of a front without precipitation. A shallow centre of low pressure in the front passed over northern Quebec, causing only an overcast sky and no rainfall at Ottawa. The morning of August 9 was clear but hazy. Cirrus- and alto-stratus and cumulus clouds appeared to form in the afternoon with southerly winds and still considerable
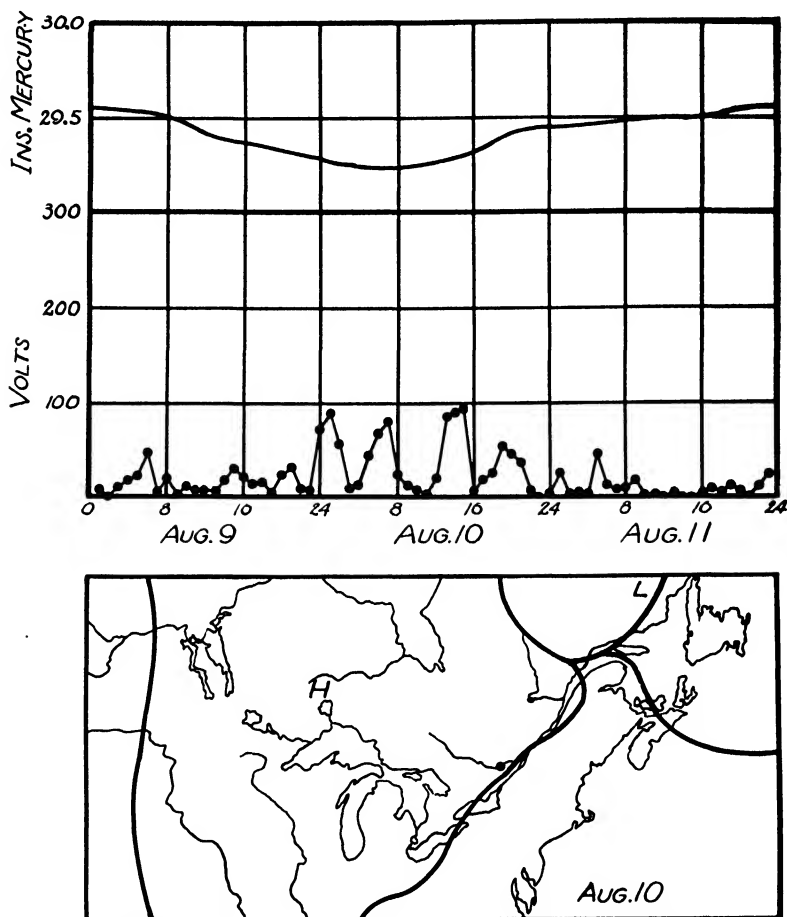
FIG. 6.   *Potential gradient disturbances and weather map, August 9-11, 1936, country station.*

haze (visibility about 7). On the morning of August 10 the wind had shifted to NW, the sky remained mostly overcast until late afternoon when it became practically clear, and visibility improved (about 9). The potential gradient shows disturbances not of very great magnitude; most of the time the sky was cloudy. As some rather large cumulus clouds were noted it is possible that part of this disturbance was due to charged clouds, but with the data available it is impossible to separate the effect of charged clouds from increased mixing due to turbulence at the passage of the front.

Fig. 7, September 22 to 25, 1936. Country Station

On September 22 at 8 a.m. there was a weak centre of high pressure over the southeastern states and another north of Lake Huron. The movement of air was from the south, as a warm front was indicated on the map for September 22 (not shown) running east and west through Lake Huron north of Ottawa. On September 23 the sky was clear of clouds with light south wind and considerable haze. The warm front had moved farther north, its position being shown on the map for September 23. A low pressure centre
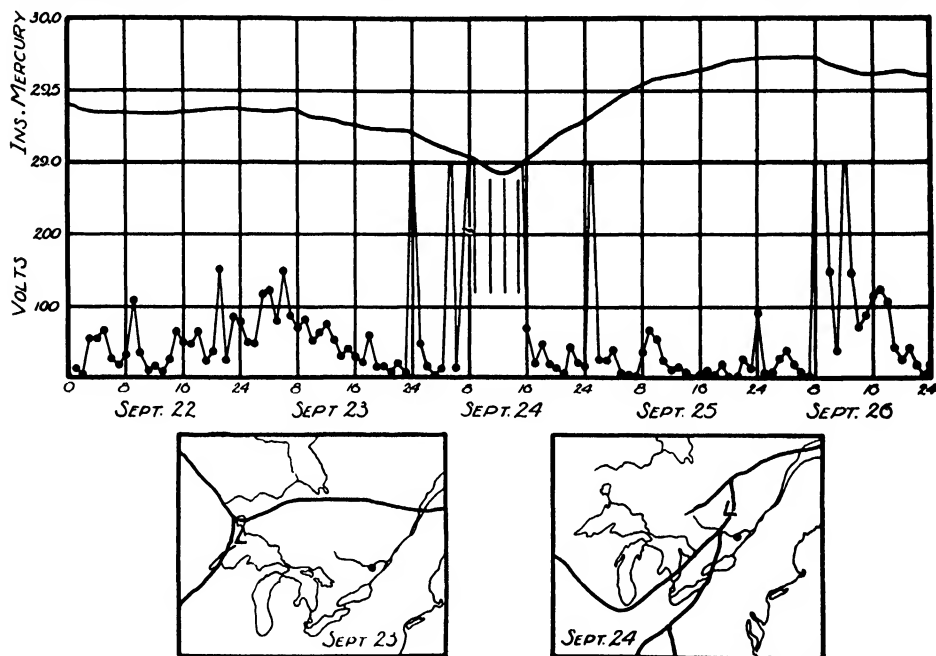
FIG. 7. *Potential gradient disturbances and weather map, September 22-26, 1936, country station.*

was moving in from the west. An air mass moving up from the south is not very usual in this part of the world, and the potential gradient was in a slightly disturbed state as the figure shows, even though there was no near frontal disturbance. Whether or not this disturbance in the potential gradient is due to the effect of a fundamental difference in the electrical characteristics of an air mass moving up from the south, in that it would be more moisture-laden, or the effect of greater density of population, is uncertain. The history of this air mass is probably different from that of the more usual mass moving in from the northwest only, in that it has gone farther south and then receded. The depression moving in from the west passed on September 24, accompanied by the usual potential gradient disturbance. Rain flurries and thunderstorms were noted on the 24th. By the morning of the 25th the sky was clearing again and the wind was NNW as a centre of high pressure covered most of the eastern part of the continent.

.   The potential gradient variation on the 26th is included in this figure to show an effect similar to that noted in Fig. 6, namely, a disturbance in the potential gradient at the centre of an anticyclone during fine weather when the sky was clear.   This occurred only a few times in the four months during which the country station was operated.   In this particular case the change in wind direction as the centre of high pressure passed was from a north-westerly direction to a southeasterly direction.   As Ottawa and Hull lie southeast of the station it is not unlikely that this disturbance was due to pollution from those cities.

Fig. 8, October 9 to 13.   Country Station

On October 9 at 8 a.m. the weather map showed a complicated system of fronts to the northwest of the Great Lakes.   A centre of high pressure was located just south of Ottawa.   Early in the morning of the 9th the electro-
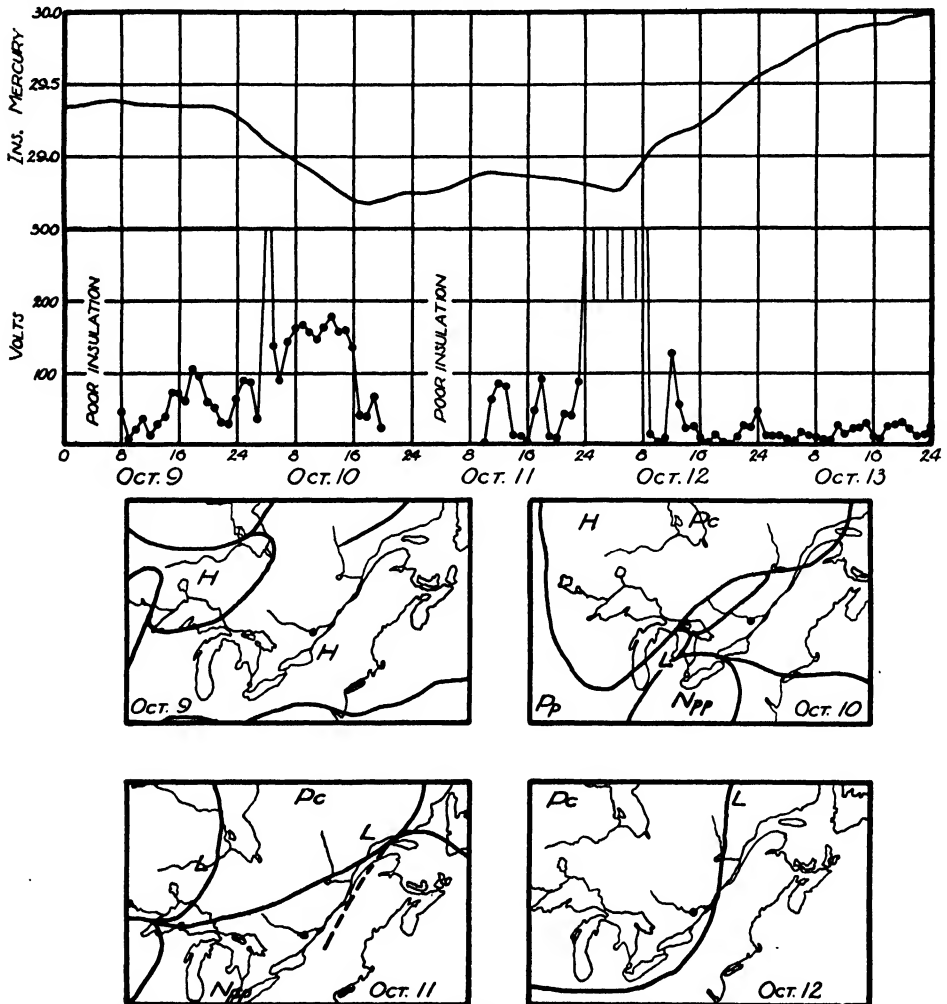
FIG. 8.   *Potential gradient disturbances and weather map, October 9-13, 1936, country station.*

meter was grounded so the record is incomplete. The sky was clear on the morning of the 9th; cirrus- and alto-cumulus clouds formed in the afternoon. The potential gradient became disturbed as the barometer started to fall rapidly, and on the morning of the 10th the sky was overcast and rain was falling. During the afternoon the sky became broken, and showed some towering cumulus clouds, and there were rain flurries. The system of fronts that passed, as is shown by the map for the 10th, is too complicated for detailed analysis. The potential gradient disturbance was not as great as usual for so near a passage of a centre of low pressure, as the electrometer fibre was driven off the scale only for a short period. During the night of the 10th rain fell steadily and the insulation broke down. During the 11th the sky was overcast with stratus clouds, but the visibility had become very good and fresh westerly winds were blowing, typical of the weather after the passage of a front. However, another front was approaching, which passed early in the morning of the 12th. Some snow fell and the potential gradient was disturbed. After the passage of this front the barometer rose very rapidly, the sky was clear except for numerous small fracto-cumulus clouds (visibility 9) and strong northwest winds were blowing. This situation continued throughout the 13th and the potential gradient deviation from the mean was abnormally low and steady.

Fig. 9, January 11-15, 1935. Laboratory Station

A front had passed late on the 10th, and the barometer was rising rapidly on the 11th as a centre of high pressure moved in from the northwest. The sky was clear with northwest winds and the potential gradient correspondingly undisturbed. On the 13th the anticyclone was to the north of Ottawa as shown on the accompanying map. The potential gradient became disturbed as the centre of high pressure passed and remained disturbed until after the passage of the front. This is typical of its behavior at the laboratory station, that is, in most cases the potential gradient became disturbed as the wind shifted from northwestern to the eastern or northeastern quadrant. At the country station the potential gradient in most cases did not become disturbed until the new front was sufficiently near to have nimbus clouds overhead. In the present case snow started to fall about noon on the 13th though the sky was overcast all morning. The front passed about midnight on the 13th and the potential gradient became normal shortly afterwards. On the morning of the 14th the sky was clear except for some cirrus clouds and the visibility very good. The weather map showed a large anticyclone covering most of the continent. This situation did not last long as a weak front formed in the anticyclone. The map for the morning of the 15th (not shown) shows a centre of low pressure over Lake Huron. The corresponding barometer depression and disturbed potential gradient is shown in the figure. Again in this case the potential gradient disturbance started at the time of maximum barometer pressure and lasted until after the passage of the front.
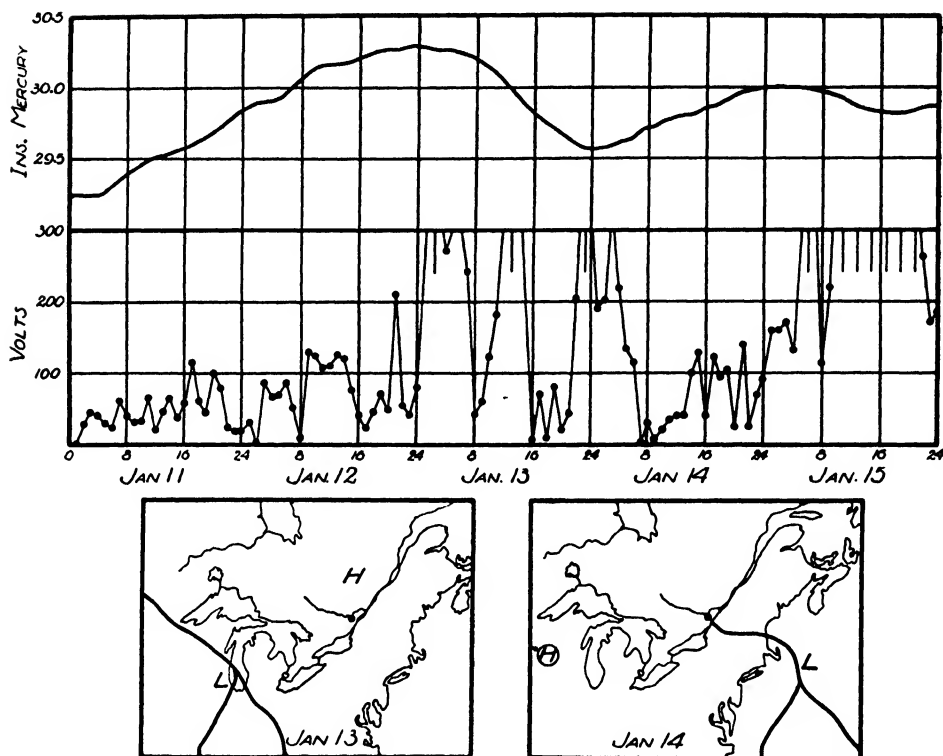
Fɪɢ. 9.   *Potential gradient disturbances and weather map, January 11-15, 1935,*
laboratory station.

The explanation of the difference between the time of start of the disturbance in the potential gradient at the two stations is considered to be in the location of the laboratory with respect to the surrounding residential area.   As mentioned before, winds in the north to west quadrant should not bring pollution.   This will be shown in more detail later.

Fig. 10, April 28 to May 1, 1935.   Laboratory Station

On April 27 a barometric low was approaching from the west, the centre of which passed north of Ottawa early on the 28th as shown by the barometer record and the accompanying map.   The low involved the movement of two or three fronts, the last of which appeared to pass during the morning of the 28th.   The sky on the 28th was partly overcast with fracto-cumulus clouds, the air clear, the wind northwest.   The potential gradient disturbance passed with the front, but as another low was forming to the west of the Great Lakes it did not remain undisturbed for long.   The potential gradient disturbance associated with the low started even before the barometer reached a maximum, and it remained disturbed until well after the passage of the front on the 30th.   The map for the 29th is not shown, as it adds but little to the description..   The system of fronts which was over the eastern states

and Canada on the 28th had passed out over the Atlantic. The low west of the Great Lakes had moved over Lake Superior and Lake Huron and had developed a little longer occlusion. There was considerable rain during the afternoon and night of the 29th, so much that the insulation failed for a few
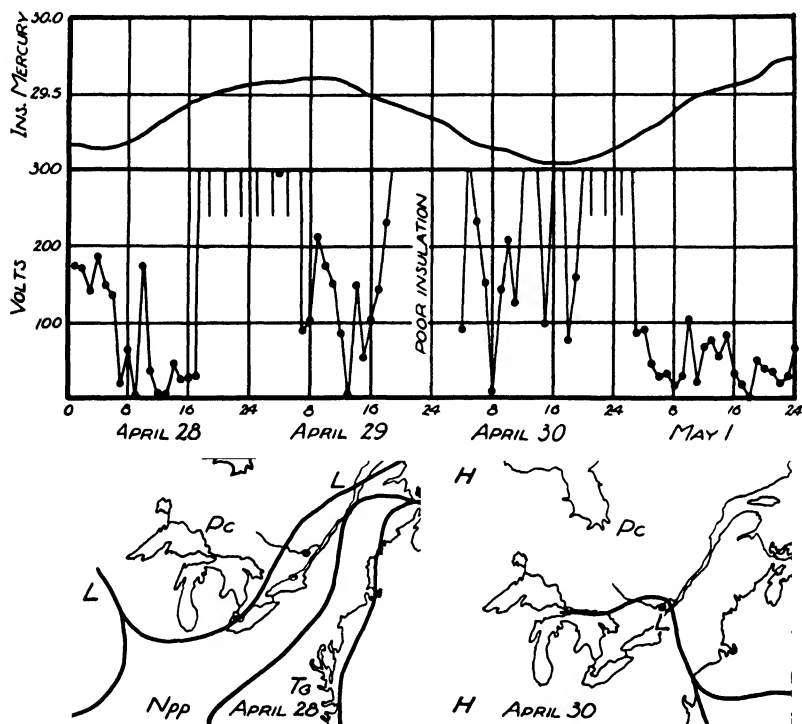
FIG. 10. *Potential gradient disturbances and weather map, April 28-May 1, 1935 laboratory station.*

hours. During the 30th, precipitation also fell intermittently, sometimes as snow. The front passed early on the 30th; the bent back occlusion shown on the map for the 30th kept the weather and the potential gradient disturbed until early on May 1. The sky cleared during the morning of the first with a fresh west wind and the potential gradient deviation became steadily low, typical of polar continental air moving in from the northwest.

Fig. 11, June 22 to 25, 1935. Laboratory Station

In this case the weather maps showing the position of fronts were not consulted. The barometer, the usual daily weather map showing centres of low and high pressure, etc., the potential gradient record, and weather notes, tell what was happening. On the 22nd at 8 a.m. two centres of low pressure were over the lower St. Lawrence and central Quebec. Rain fell steadily during the morning, so much so that the insulation failed, and during the afternoon the weather cleared—typical of conditions after the passage of a front. On the morning of the 23rd the sky was still overcast and rain flurries

continued throughout the day with very little wind. The potential gradient disturbance cleared about midnight on the 22nd, but minor disturbances appeared during the 23rd probably owing to rain flurries. The weather map for the 23rd showed a large anticyclone over the central United States which
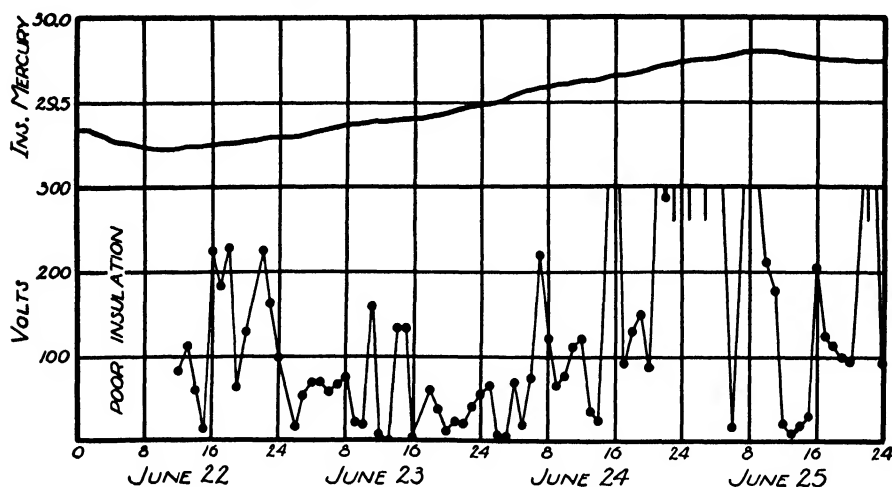
FIG. 11. *Potential gradient disturbances, June 22-25, 1935, laboratory station.*

was gradually spreading over the eastern half of the continent, as was shown by the slow rise in the barometer. The sky was still partly overcast with cumulus clouds on the 24th but the visibility was excellent. The potential gradient became disturbed on the 24th sometime before the maximum in the barometer was reached. This again was probably due to the fact that the movement of air was from the southwest and the effect of pollution from the city would be expected.

Conclusions

In summary of the results obtained at the country station it is apparent that practically every potential gradient disturbance of any magnitude may be traced to local meteorological conditions. The time at which a potential gradient disturbance starts or stops with respect to the time of passage of a cold front varies so much that no definite rule can be made about it. Usually the potential gradient becomes disturbed several hours before the passage of the front and the disturbance lasts until several hours after the front has passed. Major disturbances in the potential gradient, as would be expected, occur during rain and thunderstorms, but disturbed periods are by no means limited to the times of precipitation. Disturbances when no rain falls do not appear to be as violent as those during rain, but as data giving the times during which precipitation fell at the station are lacking no definite conclusions in regard to this point can be drawn. Apart from times of precipitation the disturbances are due to changes in the ionic equilibrium caused by increased turbulence at a front, or by charges developed in clouds which have not developed into thunderstorm, or are due perhaps to nearby thunder

clouds. Whether electric charges may develop in clouds from which precipitation is not falling is uncertain. Sil (17) finds that the potential gradient is disturbed when cumulus or alto-cumulus clouds are forming overhead. If electric charges are formed in such clouds which have not developed to such an extent that drops of water of appreciable size are formed, some new theory of the production of electric charges in thunderstorms other than Wilson's theory (21), which involves the motion of drops of water, is required.

The duration and magnitude of the potential gradient disturbance appear to depend on the slope of the frontal surface, the strength of the front, and whether a centre of low pressure passed near by. There is probably at least a quantitative relation between the magnitude of the potential gradient disturbance, the duration of the disturbance, and the strength of the front. In the summer months, winds as a rule are lighter and the barometer variation is smaller than in autumn and winter periods. A corresponding difference in the potential gradients would be expected. The period during which the station was operated (four months) is hardly long enough to give much information on this point, but the potential gradient disturbances do appear to be off the scale oftener and for longer periods in the autumn months than in the summer. That the total disturbed time is greater in the autumn than in the summer is shown by the figures in Column 6 of Table I, the part referring to the country station. The corresponding figures obtained at the laboratory station, because of its geographic relation to the city, represent more the percentage of winds in the northwest quadrant than the effect of the passage of fronts.

To study quantitatively the relation of potential gradient to the passage of fronts the following data are noted. Dividing the four months during which the country station was operated into periods between the passage of anticyclones of sufficient strength to produce an undisturbed potential gradient for a day or more, one finds:

Twenty-six cases where the potential gradient disturbance coincides with the passage of a front or fronts in the general way outlined above.

Nine cases where information is incomplete owing to unsatisfactory operation of the apparatus or incomplete meteorological information, but agreement appears likely if information were complete.

Three cases where there was no clear relation between potential gradient disturbances and fronts. In two of these the front was so weak that no appreciable barometer variation was noted. In the third case a definite front passed with no potential gradient variation.

Four cases where a disturbance occurred at the centre of an anticyclone as noted in the description of Figs. 5 and 7.

While this work was in progress, Schou (15) reported some work in which negative conductivity and potential gradient were studied in relation to the passage of fronts. Considerable emphasis was laid on the discontinuity in negative conductivity at the passage of the fronts, but no study was made of disturbances in potential gradient at such periods. Cooper (6) has inter-

preted measurements of potential gradient disturbances spread over a number of years to indicate a correlation between the passage of sun spots and disturbances in potential gradient.   In the case of the present observations the disturbed periods coincided so well with meteorological conditions that it seemed unnecessary to look for such an improbable effect.

In conclusion, there is one other effect which is interesting in that it confirms the explanation, given by the author, of the differences between the effects found at the country and laboratory stations.   If one averages the deviations from the mean values over periods of say 12 hr. and plots these on a polar diagram, the basis for which is wind direction, the diagram shown in Fig. 12 is the result.   The average is taken for 12-hr. periods from 1 to 12 hours
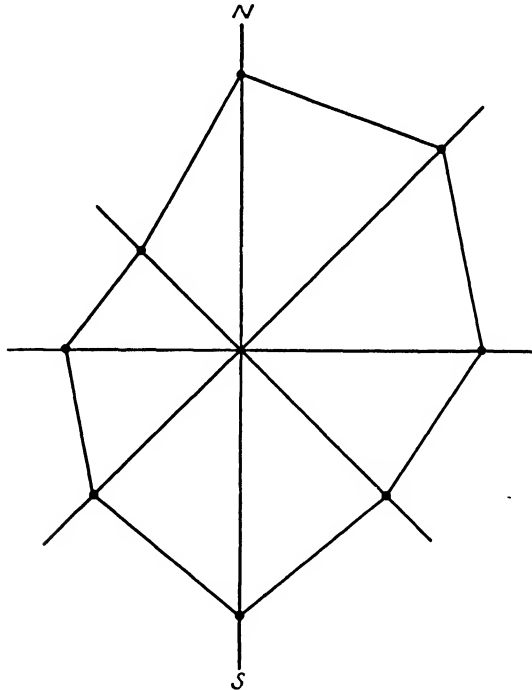
FIG. 12.   *Mean deviation plotted against wind direction.*

each day that the laboratory station was operated.   Where the electrometer fibre is off the scale the deviation used in averaging is arbitrarily taken as 350 volts.   These are divided into eight groups in accordance with the wind directions given on the 8 a.m. daily weather maps.   The average deviation is then found for each group.

Now consider the minimum deviation, *i.e.*, when the wind is northwest. Take this to represent the magnitude of potential gradient disturbances under most stable conditions and subtract it from the value when the wind is in other directions.   A figure shown by the full lines in Fig. 13 is obtained.   The broken curve represents a rough estimate of the population density in the cities of

Ottawa and Hull plotted with respect to direction from the laboratory.   The estimate is made merely by measuring to the outskirts of the region covered by the cities on a large scale map of the surrounding area, park and uninhabited areas being omitted.   The measurements are plotted to a scale which makes the two curves fit at one point.   The similarity between the two curves in the W,SW,S, and SE directions, and the differences in the N,NE, and E
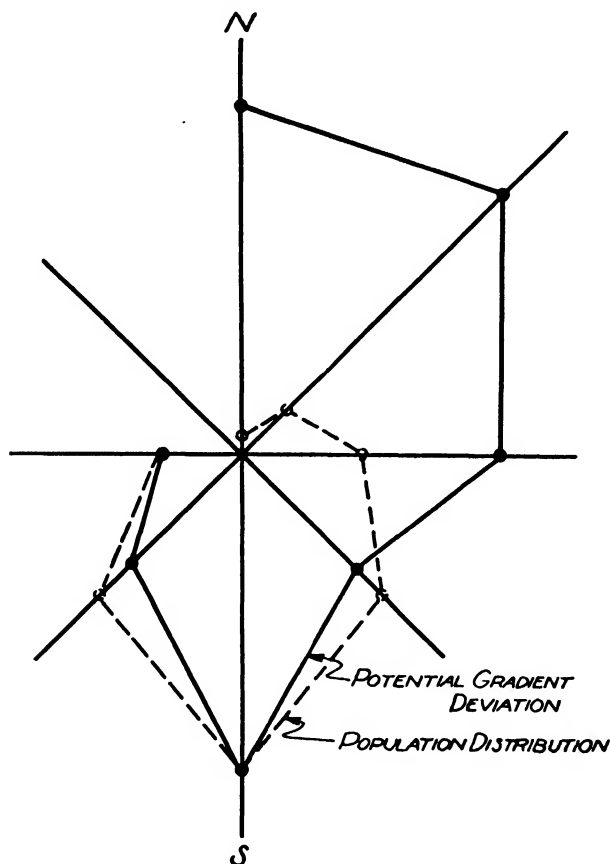
FIG. 13.   *Potential gradient disturbances plotted against direction of wind compared with population distribution.*

directions are apparent.   The explanation lies in the geographic relation of the laboratory and the prevailing direction of winds in fine and stormy weather.   Where the shape of the potential gradient deviation curve is similar to the population distribution curve, the potential gradient disturbance can be blamed on city pollution.   When stormy weather typical of an approaching front with a nearby depression is approaching, the wind is usually in the north to east quadrant.   The value of the point representing disturbances from the north may be enhanced somewhat by the presence of the laboratory heating plant.   Similar curves for the four seasons show slightly different shapes.

Acknowledgments

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PROBABILITY EXPERIMENTALLY INVESTIGATED[1]

By A. L. CLARK[2]

Abstract

This paper is the third and last of a series of papers on an experimental investigation on probability. Steel balls were dropped on a horizontal steel plate in which holes were bored in a regular pattern. The probability that a ball will pass through a hole without touching the plate is calculated from the known data and found to be 0.3554 ± 0.0005. The experimental value of the probability or the ratio of free passages to the total number of balls dropped is 0.35557. The agreement is very good. The numbers of runs of various lengths were calculated and compared with the actual numbers of these runs, again with good agreement. π may be calculated from the experimental value of the probability.

In two earlier papers (1, 2) the theory of an experimental study of probability and the apparatus used were described. The results of the observations up to 250,000 events were indicated and some conclusions were drawn. In the work described in this paper the number of observations has been increased to the half million mark.

Briefly, the experiment involves the dropping of steel balls on a horizontal steel plate pierced with circular holes arranged in a regular hexagonal (triangular) pattern. The observer records whether or not each ball passed through a hole without contact with the plate. A microphone attached to the plate makes detection of a contact easy.

The probability that a ball will pass through without contact is

$$P = \frac{2\pi(R - r)^2}{d^2\sqrt{3}} ,$$
(1)

where R and r are the radii of the holes and balls respectively, and d is the distance between the centres of adjacent holes. Substituting the measurements of these quantities in Equation (1) and making the correction for departure of the paths from the vertical (1) the calculated probability is

$$P = 0.3554 \pm 0.0005 .$$

Of the 500,000 balls dropped, 177,785 passed through freely which gives for the experimental value of the probability

$$P = 0.355568 .$$

As will be seen, the agreement between the values of P is very close, better than the accuracy of the measurements of diameter and centre distances could be expected to give. Since the experimental value of P may be regarded as a very accurate approach to the true value of the probability, the close agreement between the experimental and calculated values of P indicates that the errors in measurements neutralize each other to some extent.

The value of P to date* oscillates erratically so that the value at the end of any series may not be the best value. The end of the series may show an abnormally high or low value depending on what has happened during the last part of the series. A process of interpolation (explained in the earlier papers) was employed to determine by judgment what would be the end value of an infinitely long series. This interpolated value is

$$P = 0.355570 ,$$

which is very close to the end value and is to be taken as the best value assignable from the data available. The last events of the series happen to run well in accord with theory.

Fluctuations

The fluctuations about the accepted value of P are shown in Table I, where the experimental values and the departures from the accepted value are shown for series lengths of 25,000, 50,000, and 100,000. Similar figures are shown for the values to date by 25,000's.

TABLE I

25,000		50,000		100,000		To date by 25,000's	
P	δ	P	δ	P	δ	P	δ
.35460	−.00097					.3546	−.0010
.35732	+.00175	.35596	+.00039			.35496	+.0039
.35396	−.00161					.35529	−.0028
.35644	+.00087	.35520	−.00037	.35558	+.00001	.35558	+.00001
.35596	+.00039					.35566	+.00009
.35428	−.00029	.35512	−.00045			.35543	−.00014
.35844	+.00287					.35586	+.00029
.35292	−.00265	.35568	+.00011	.35540	−.00017	.35550	−.00007
.35576	+.00019					.35552	−.00005
.35584	+.00027	.35580	+.00023			.35555	−.00002
.35236	−.00321					.35526	−.00031
.35348	−.00209	.35492	−.00065	.35538	−.00019	.355447	−.000123
.35448	−.00009					.355388	−.000182
.35976	+.00419	.35722	+.00165			.355700	+.000130
.35352	−.00205					.355555	−.000015
.35688	+.00131	.35520	−.00037	.35621	+.00064	.355640	+.00070
.35484	−.00073					.355591	+.000021
.35516	−.00041	.35500	−.00057			.355567	+.000003
.35668	+.00111					.355630	+.000060
.35448	−.00109	.35558	+.00001	.35529	−.00028	.355568	+.000002

* *The value "to date" is the value of P from the beginning of the series to any point where P is calculated.*

The percentage maximum fluctuations are shown in Table II.

TABLE II

Series length	Fluctuation, %	Series length	Fluctuation, %
100	18.0	25,000	0.42
1000	6.4	50,000	0.049
5000	1.8	100,000	0.011
10,000	1.42	250,000	0.0006

The rapid decrease in the value of the percentage maximum departure from the accepted value of P with the series length is significant. It is easy to see why the relative departure from equilibrium conditions is negligible when we are dealing with a very large number of events occurring with perfect randomness. For example, in the case of an appreciable volume of gas under moderate pressure the departure from the mean number of collisions of the molecules with the wall or with an object immersed in the gas is too small to be noticeable. When, however, the area of the wall or of the object becomes small enough then the number of events becomes small, and the relative fluctuations about the mean become large and effects become noticeable as with the Brownian movement.

The Value of π

In the first paper, the value of the probability was taken as 0.35556. This value when inserted in Equation (1) gives $\pi = 3.143$.

It must be remembered that the accuracy of the ratio of P to π is known only to five parts in 3500. Therefore, the value of π can legitimately be calculated only to the same accuracy. The value of P is now believed to be 0.355570. This value when substituted in Equation (1) gives

$$\pi = 3.145 .$$

If, however, we were to search the record of the observations we might, and probably would, find points in the series such that if we were to begin and end at these points and calculate the value of P, a very accurate value of π might result from substitution in Equation (1). For example, the value of P at the end of the series, stopping at 275,100 events, is 0.35525. This value when substituted in Equation (1) gives

$$\pi = 3.14167 .$$

No doubt a more favorable stopping point might be found. It is, however, not worth while to find such points as the value of π, deduced from the value of P, so found, would be misleading. The best value which can be assigned to π from this experiment is 3.145. This, while not very different from the previous value, is not quite as good. This means that the unavoidable inaccuracies in the measurements of R, r, and d are present in the calculation.

It is suspected that the remarkable determinations of P obtained by some observers from an experimental examination of Buffon's problem are not above suspicion.

Probability Curve

As before, the values of P by 100's were tabulated and the number of times each value of P appears in the table was plotted against P. The resulting
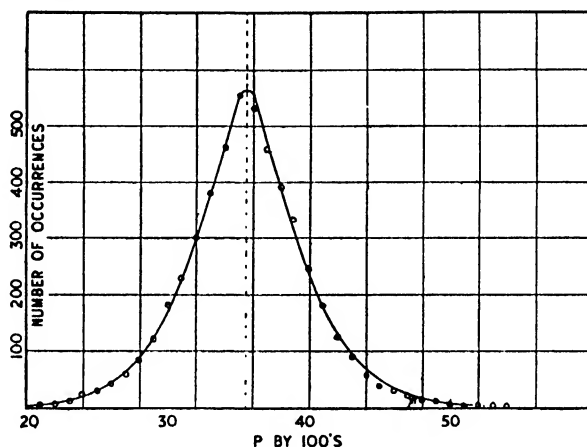
FIG. 1

curve is shown in Fig. 1 and is a very good picture of the ordinary probability curve. The points lie very well on the curve and it is very nearly symmetrical about the value $P = 0.3556$.

Sequences

When the number of events is large, the sequences or the continuous runs of favorable cases (free passages) may be calculated from

$$N = nP^k , \tag{2}$$

where k is the length of the run, N the number of times a run of length k appears, and n the total length of the series taken. The number of times each run actually occurred were counted and the results are shown in Table III. The columns in order show the sequence length, the calculated value of N, then the counted numbers of times the sequences appeared for series lengths of 100,000, and finally the calculated and observed values of N for the series 500,000.

Examination of the table shows clearly that the value of the experimental probability for a series length of 100,000 changes but little from series to series. Longer series produce even better agreement. The numbers of runs of 4, 5, 6, are not in very good agreement with theory. It must be kept in mind, however, that we are dealing, in the runs, with a relatively small number of events of the kind under discussion (runs) and the agreement may be disappointing. The fine agreement for shorter and longer runs must be regarded as fortuitous. The first 100,000 gave extraordinary agreement

TABLE III

Runs	100,000's observed						500,000	
	N, Calc.	1st	2nd	3rd	4th	5th	N, Calc.	N, Obs.
1	35557	35558	35540	35536	35461	35529	177785	177785
2	12643	12359	11532	12722	13283	12693	63215	62559
3	4496	4655	4195	5181	5378	5015	22477	24482
4	1598	1489	1223	1969	2088	1801	7992	8579
5	568	572	405	865	967	769	2841	3578
6	202	191	82	333	367	279	1010	1252
7	71	74	18	137	131	93	359	453
8	25	33	5	45	38	25	128	146
9	9	17	0	13	11	5	45	46
10	3	9	0	3	4	0	16	16
11	1	5	0	1	2	0	6	8
12	0.4	3	0	0	0	0	2.0	3
13	0.1	1	0	0	0	0	0.7	1

between observed and calculated values of N. The second series of 100,000 was very disappointing after the success with the first. It is to be expected, however, that while some series will show good agreement others will not.

The failure of the results to accord with those calculated from Equation (2) need not cast discredit on the formula, although it is always a question how reliable any formula for a probable value may be considered. Sometimes it is almost certain to fail to give what is expected. This is the nature of probability. In order to give a more adequate test a much longer total series must be taken.

It has been pointed out in this series of papers that while in a general way the results are entirely in accord with theory, there are many unexpected peculiarities. For example, and it is perhaps the most significant single result, a run of 13 appeared in the nineteenth thousand, whereas such a run should appear about once in a million trials. The often suggested waiting a long time for the improbable to happen may not be necessary and on the other hand, it may not appear, even in a run many times the length thought necessary--indeed it may not appear at all in a finite series. The practice so often employed in sampling of basing conclusions on relatively few observations may in some cases give results far from the truth. Generally speaking the larger the number of events in a series, the more assurance one may have that conclusions drawn from a study of this series are reliable.

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ABSORPTION STEP-WEAKENERS OF ANTIMONY[1]

By G. O. Langstroth[2] and D. R. McRae[2]

Abstract

It is of advantage to the spectroscopic analyst to have a means of quickly preparing a step-weakener of any required characteristics. A method has been developed in which antimony films are deposited by thermal decomposition of the trihydride. The apparatus required is simple, and a multi-step weakener may be made in 20 min. The films are nearly neutral below λ 4000Å. Their optical density is quite uniform, and they are sufficiently strong for all practical purposes. For high precision work, the construction of the weakener must be such that undesirable interference effects are avoided. A consideration of the theory of interference phenomena in light transmitted through thin plates suggests several possible methods of construction. Some of these have been adopted and have been found to be satisfactory in practice.

In quantitative spectroscopic analysis it is often desirable to photograph the spectrum of a sample in such a way as to obtain a series of graduated steps of known relative intensity with a single exposure. The photographic blackening of the spectral line in which one is interested will then lie in the "normal exposure region" for some particular step, and a precise measurement of it can be made. This procedure often results in a considerable saving of time and effort, and indeed may be a necessity in certain problems. Three common circumstances in which it is especially useful are: (1) when it is desired to analyze for several elements in each sample, (2) when the concentration of the investigated element varies widely from sample to sample, and (3) when results of the highest accuracy are not required. In the first, one exposure is sufficient for a complete analysis, whereas with the ordinary technique several exposures may be necessary, and these cannot be made if the sample is small. In the second, it is not necessary to take a trial plate for each sample in order to determine suitable conditions for exposure, as is the case with the ordinary technique. In the third, an estimate of the concentration may be made by observing at which step the blackening of the investigated line reaches a standard arbitrarily set value.

The spectrum may be photographed in a series of steps of graduated intensity by placing an absorption step-weakener immediately in front of the spectrograph slit. Rotating step-sectors or mesh screens cannot be used with spark sources for this purpose, because the intensity of the light radiated by the atoms of the sample decreases with time during the exposure. Each problem which one encounters may require a step-weakener of special characteristics, and it is therefore of advantage to the spectroscopic analyst to have a means of quickly preparing a step-weakener of any required design.

This paper describes a method for preparing step-weakeners of antimony. The metal is deposited on a suitable surface (*e.g.* glass or quartz) by thermal decomposition of the gaseous trihydride in a tube in which the progress of

the deposition may be estimated visually or measured objectively. The apparatus required is simple and readily available in any laboratory, and a "multi-step" weakener may be made in from 15 to 20 min. The metallic films so produced are nearly neutral below λ 4000Å, and are quite uniform in density. They are strong, and no gross changes in appearance or marked changes in absorption have been observed during the three months of use which the writers have given them.

The choice of the quartz or glass plate on which any kind of film is deposited to form a weakener is important, because interference occurs between internally reflected rays in the transmitted light, except when the plate is accurately plane parallel. If the plate is badly chosen, the photographic images of the spectrograph slit exhibit intensity maxima and minima along their length, and cannot be used for intensity determinations of the highest accuracy. A consideration of the theory of such interference as worked out by Pahlen (1) suggests several ways in which this difficulty may be overcome. Perhaps the best of these is to deposit the film on a wedge-shaped plate, which is then cemented to a similar plate with Canada balsam in order to protect the film and compensate for ray deviation.

1. Deposition of the Film

The tube used for depositing the films is shown in Fig. 1. It consists of a Pyrex tube of about 3 cm. diameter drawn down to a fine jet, *J*, at one end, and closed at the other by means of a rubber cork through which runs an adjustment screw, *A*. Two side arms are blown on this tube; one is closed by the window, *W*, and the other by a rubber cork and the Pyrex tube carrying the furnace, *F*. A metal carriage, *C*, is firmly fixed in the tube so that the hole in it is directly over the furnace. The details of the water cooling for this carriage are not shown in the diagram. A flat metal slide, *E*, runs in grooves in the carriage, and may be removed from the tube by withdrawing the cork and simply pulling it out. This slide is about 2 cm. wide and 11 cm. long, and there is an opening in it which coincides with the opening in the carriage when the slide is in position. Two microscope cover slips, *M*, are fixed adjustably to the slide by spring clips so that their ends project over the opening in the slide, but leave an open strip equal to the width of the metallic film which it is desired to deposit. In addition, a metal block which carries the spring, *S*, and the adjustment
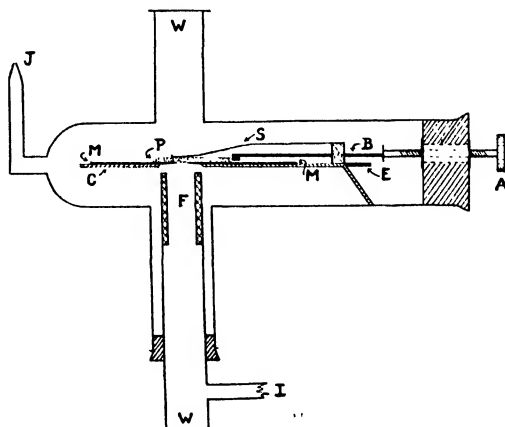
FIG. 1. *Diagram of the tube for depositing antimony films.*

rod, B, is permanently fixed to the slide. The quartz or glass plate, P, on which it is desired to deposit a film is placed on the slide as shown. It is held down on the mask, M, by the spring, and can be moved along the tube by adjustment of the screw, A.

A steady flow of a mixture of hydrogen and antimony trihydride is passed into the tube at I, and the escaping gas is burned at J. When the furnace is electrically heated to a sufficiently high temperature the antimony trihydride is decomposed and metallic antimony is deposited on the strip of the plate P which is left uncovered. When the density of the film is sufficiently great, the plate is moved along to the required position for the next step by adjustment of A, and a second film is deposited. Any number of steps of any reasonable width, and of any optical density, may be made in this way. The optical density of the film may be viewed by transmitted light at any time during the deposition by looking down through the window of the side tube. If necessary, the density may be measured objectively, but the writers have found visual estimates sufficient for their work thus far.

It should be pointed out that antimony trihydride is poisonous, and that care should be taken not to inhale appreciable quantities of it.

The furnace. The furnace is cylindrical in form with a diameter of about 1 cm. and a length of about 3 cm. The upper end of the furnace comes to within about 4 mm. of the surface of plate P. The heating element is wound on an aluminium cylinder, and is carefully covered with an asbestos cement. The cylinder cannot be made of a metal which forms an antimonide when heated (*e.g.*, copper), for then practically all the antimony is held by the furnace. The resistance of the furnace is about 7 ohms, and the current required is about 4 amp. The temperature has not been measured, but it must be sufficiently high to decompose antimony trihydride, which breaks down at 150° to 200° C.

The mask. The microscope cover slips which form the mask are about 0.3 mm. thick. They are ground down (from the under side) to a sharp edge with an angle of about seven degrees. This is done to get rid of projecting edges which disturb the lines of flow of the impinging gas which carries the metallic antimony. If it is not done the deposition is greater in the centre of the strip than near the edges.

The production of antimony trihydride. An ordinary Kipp generator containing dilute sulphuric acid and zinc, and a small amount of an antimony salt, is suitable for producing the mixture of hydrogen and antimony trihydride required. In practice 10 cc. of a 3 gm. per cent antimony solution was introduced into the zinc chamber of the generator, and generally no more was added during the life of the charge. The yield under these conditions was found by analysis to be from 0.006 to 0.02 volumes per cent antimony

trihydride in hydrogen.   The gas was bubbled through lead nitrate to remove
hydrogen sulphide, which if present resulted in the formation of yellow powdery
films (sulphides of antimony).   It was then passed through a calcium chloride
drying tube, and into the tube proper.   The rate of flow of gas generally
used was about 7 cc. per sec.   The gas was always allowed to flow through
the tube for a few minutes before the furnace was turned on, in order to wash
out the oxygen.   If this was present in appreciable quantities whitish powdery
films were formed (oxides of antimony).

2. Properties of the Films

Appearance, strength, and permanency. The films are metallic in appearance,
and when thick enough make excellent mirrors.   An enlargement of a four-
step weakener is shown in Plate I, *a*.   The films are strong enough for all
practical purposes, and may be cleaned without damage by swabbing with
cotton wool dipped in some suitable cleaning liquid.   They appear to be
quite stable, as might be expected from a consideration of the chemical
properties of antimony.   The authors have not detected any signs of cracking
or other gross change, or of marked change in the absorbing power, during
the three months in which the films have been in use.

Uniformity.   If proper precautions are taken, as mentioned in the preceding
section, the films are quite uniform in density.   This point is illustrated by
the transmission measurements for a four-step weakener given in Fig. 2.
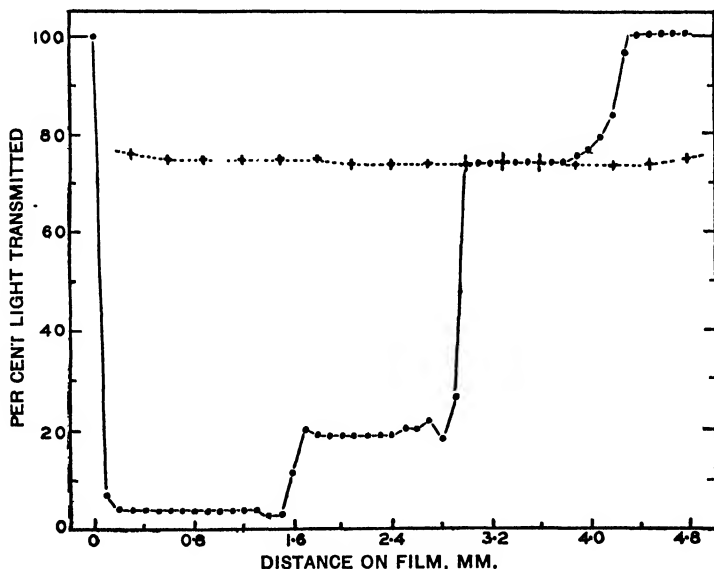
Fig. 2.   *Degree of uniformity in the optical density of the steps of a four-step weakener.
The points indicated by ● represent measurements taken across the steps; those indicated by +
represent measurements taken along the length of a step.*

Wave-length absorption characteristics.   The films are nearly neutral below λ 4000Å, but absorb less strongly for longer wave-lengths.   The results of photographic transmission measurements made on two films are given in Fig. 3.
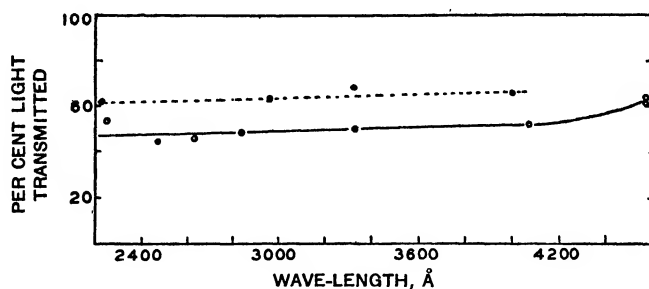
FIG. 3.   *Transmission-wave-length curves for antimony films.*

3. The Construction of Absorption Weakeners

In the early stages of this work it was observed that the spectral lines almost always exhibited intensity maxima and minima along their length when thin microscope cover slips (with or without metallic films) were placed before the spectrograph slit.   Subsequent investigation indicated that these effects were due to interference between internally reflected rays.   Plate II, *a* and *b* illustrate the type of effect observed.

It is obviously out of the question to photometer lines consisting of distinct intensity maxima and minima with the expectation of attaining a high degree of precision in the intensity measurements.   Moreover, in the use of a wedge-weakener the validity of intensity measurements depends on the validity of the assumption of a one-to-one correspondence of points on the line with points on the wedge.   If interference occurs this correspondence is effectively destroyed, at least to an extent determined by the separation of the maxima. It is, therefore, important to devise a means of overcoming this difficulty. It is rather surprising that there appears to be no mention of it in the literature on absorption weakeners.

The theory of the interference phenomena which occur when light is transmitted through thin plates has been worked out by Pahlen (1).   When a bundle of approximately parallel light rays is incident at an angle ϕ on a thin wedge-shaped plate of mean thickness D and angle ϵ (with the plane of incidence perpendicular to the end of the wedge), sharp interference patterns are expected at a distance E from the plate surface, such that,

$$E = \frac{D}{\epsilon} \frac{\sin \phi \cos^2 \phi}{\eta^2 - \sin^2 \phi} \tag{1}$$

where η is the refractive index of the plate material.   This interference plane passes through the apex of the wedge at an angle α with the wedge surface, where,

$$\tan \alpha = \frac{\sin \phi \cos^3 \phi}{\eta^2 - 1 + \cos^4 \phi} \ . \tag{2}$$

Sharp interference will also be found in planes parallel to this one and at distances e_ρ from it, where,

$$e_\rho = \frac{\lambda}{2\epsilon^2} \cdot \frac{\sin \alpha}{\sin \phi \cdot \cos (\phi - \alpha)} \cdot \rho \qquad \rho = \pm\tfrac{1}{2}, \pm1, \pm\tfrac{3}{2}, \ldots \qquad (3)$$

The interference is virtual when ρ is negative.   When $\phi = 0$,

$$e_\rho = \frac{\lambda}{2\epsilon^2\eta^2} \rho \cdot$$

In all these planes the interference maxima will be separated by a distance h, whose projection, s, on a plane normal to the direction of the rays will be,

$$s = \frac{\lambda}{2\epsilon} \frac{\cos \phi}{\sqrt{\eta^2 - \sin^2 \phi}} \cdot \qquad (4)$$

These equations describe qualitatively the effects that have been observed, but the authors have made no attempt to test them in an absolute quantitative sense.   The following table, calculated by means of the above equations, shows the expected magnitude of the various variables for interference in a quartz plate.

TABLE I

ϵ, sec.	ϕ, min.	D, cm.	E, cm.		e_1, cm.		s, mm.	
			λ1980	λ5890	λ1980	λ5890	λ1980	λ5890
10	10	.03	.64	.75	740.	2250.	1.2	3.8
		.3	6.4	7.5	740.	2250.	1.2	3.8
	180	.03	11.3	13.4	740.	2250.	1.2	3.8
		.3	113.	134.	740.	2250.	1.2	3.8
3600	10	.03	.0018	.0021	.0059	.020	.0034	.011
		.3	.018	.021	.0059	.020	.0034	.011
	180	.03	.033	.038	.0059	.020	.0034	.011
		.3	.33	.38	.0059	.020	.0034	.011

The theoretical considerations suggest that there are three ways in which the undesired effects may be eliminated; (1) by using an accurately plane parallel plate on which to deposit the film, (2) by using a "thick" plate at an appreciable angle of incidence so that the first interference plane falls some distance behind the spectrograph slit, and (3) by using a wedge-shaped plate of sufficiently large angle to bring the interference maxima so close together that they are not resolved by the grain of the photographic plate.

The first of these alternatives is apt to prove expensive.   In accordance with the second, the authors have successfully made weakeners which are useful down to λ 3000Å.   The required film is deposited on a microscope cover slip, which is then cemented to a metal ring to form one side of a water cell.   A second cover slip without a film is cemented to the other side of the

ring to form the complete cell. This is filled with water and sealed off. Its disadvantage is that the film is unprotected. When the film was coated with a pyroxalin solution such as is used for rock salt prisms serious interference effects occurred owing to internal reflections from the pyroxalin-air and pyroxalin-metal surfaces. It is questionable whether the success of these weakeners is due to their thickness or to the fact that the angle between the two external surfaces is appreciable. Some pieces of quartz 3 mm. thick caused striking interference patterns; this rather inclines one to the latter view. Moreover, if by chance such a weakener is set up at exactly normal incidence, the first interference plane will lie directly on the surface, and if this is against the slit, interference phenomena should be observed in the photograph.

Probably the best method of construction is that of the third alternative. The film is deposited on a wedge-shaped plate of angle, say, 3°. The separation of the interference maxima will be 0.0022 mm. for λ 5890Å, and this distance will not be resolved on the photographic plate with a spectrograph of ordinary magnification. In order to protect the film and to compensate for ray deviation, a second similar plate without a film is cemented to the first. This construction was found to be entirely satisfactory.

Acknowledgment

Reference

1. PHALEN, E. V. D. Ann. Physik, 39 : 1567-1589. 1912.

PLATE I
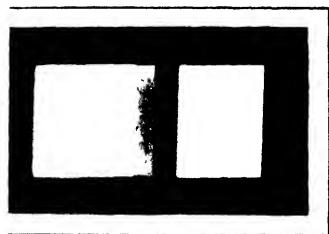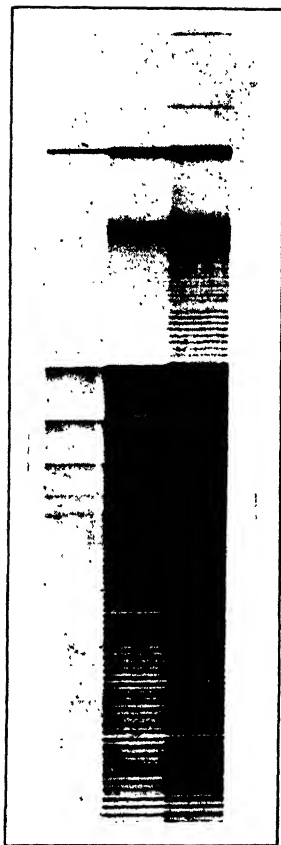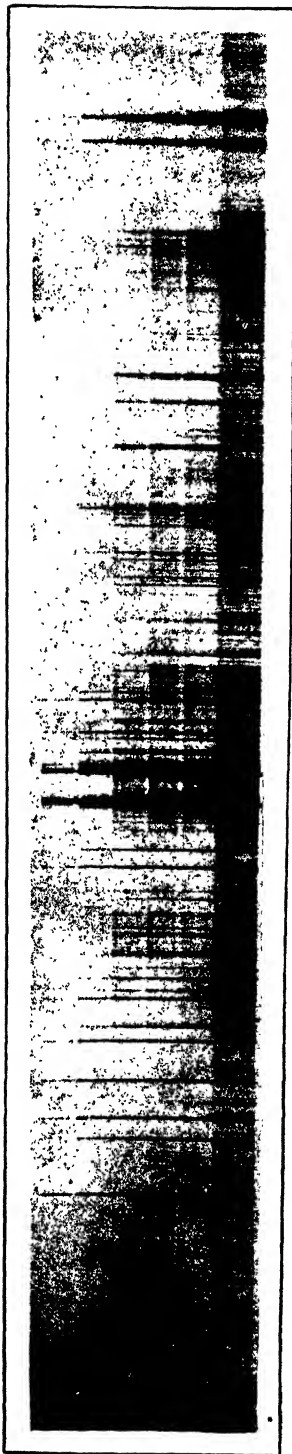
a. A photograph of a four-step weakener. The actual width of each of the steps is about 1.2 mm. *b.* The spectrum of the cyanogen bands at λ 3883Å taken with a three-step weakener. *c.* The spectrum of the copper arc from λ 2860 to 4100Å taken with a six-step weakener. The strong lines in the centre are, 3247.6 and 3247.0 Å.

PLATE II

a.

b.
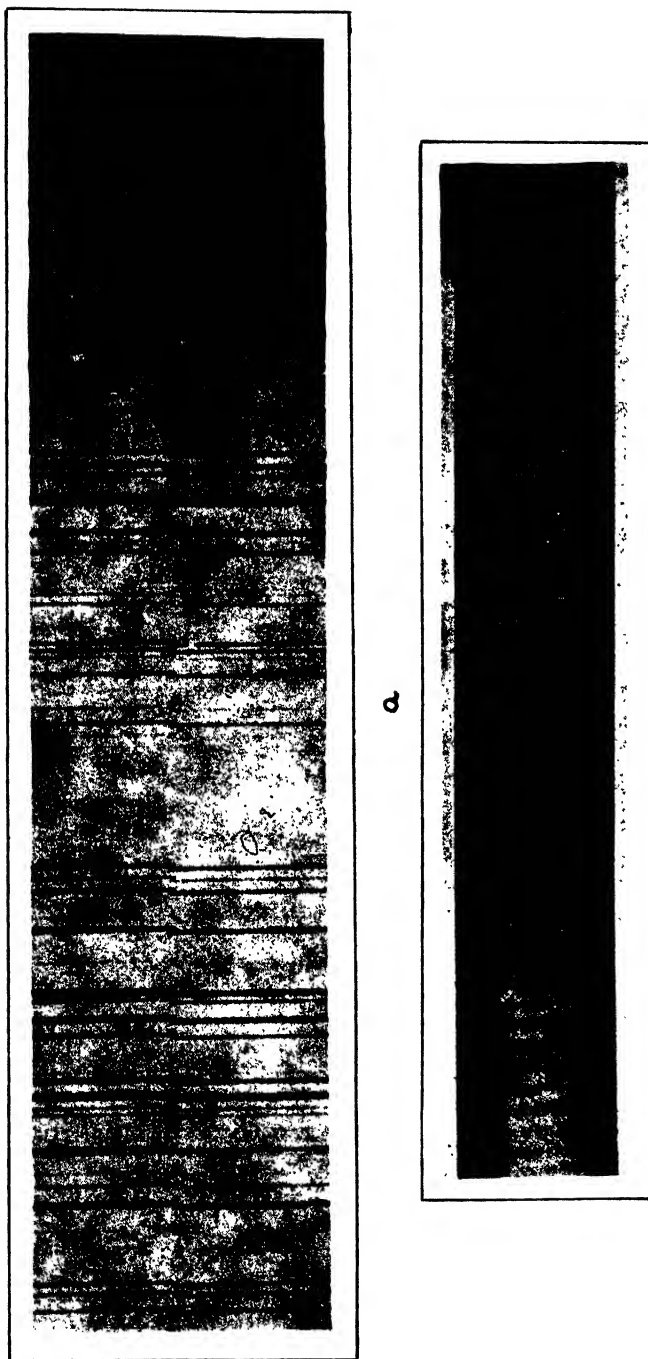
a. Two exposures showing interference effects in line spectra. These effects are of the type discussed in Section 3. They were obtained by placing an ordinary microscope cover slip (without a film) before the slit of the spectrograph. The direction in which the cover slip showed a deviation from plane parallelism was determined, and for the first exposure this direction was set parallel to the length of the spectrograph slit. For the second exposure the cover slip was rotated through a fairly large angle from the first position. In both exposures the surface of the cover slip was kept perpendicular to the collimator axis. The interference maxima in the first exposure are much closer together than in the second exposure, which is in accord with theoretical expectations. The region of the spectrum shown in the photograph is near λ 3700Å. The magnification of the enlargement is about 5×. An interesting feature shown in this plate is the rather rapid change in the spatial position of a maximum when the wave-length is changed. (See Pahlen's article.)

b. Interference effects in the continuous spectrum emitted by a band lamp. These effects were obtained when a cover slip was placed before the spectrograph slit. They undoubtedly have an explanation based on the considerations of Section 3. The less exposed strip in the centre of this photograph is due to the absorption of the antimony film which was deposited on the cover slip. The spectral region shown is near λ 3600Å. The magnification of the enlargement is about 5×.

THE SPECTRUM OF α-LYRAE[1]

BY J. D. BABBITT[2]

Abstract

Results are given of the measurement of spectrograms of the star α-Lyrae taken at the Dominion Astrophysical Observatory, Victoria, B.C. One hundred and fifty-six lines were found in the spectrum and 147 of these were identified. Microphotometer tracings of the Balmer series and of the stronger metallic lines were measured and the profiles were plotted. The total absorptions were obtained from the profiles and compared with previous measurements.

Introduction

A great advance has been made, both theoretically and observationally, in the study of the profiles of stellar absorption lines since Schwarzschild first investigated the H and K lines of ionized calcium in the solar spectrum. So successful has been the attack on this problem during recent years that this method of approach has now become one of the most powerful means of investigating the atmospheres of the stars. When the problem of the formation of absorption lines in a stellar atmosphere has been fully solved and it is possible to obtain theoretical profiles, which give a satisfactory explanation of the observed lines, then shall there be a method whereby first-hand information of such properties of stellar atmospheres as temperature, pressure, and composition can be obtained. So far, however, theory has been unable to produce an adequate explanation of the observed shapes of absorption lines and much work remains to be done on this subject. As a result of this failure of theory to produce a formula capable of satisfying observation, most of the work on line profiles has been concentrated on the study of total absorptions or equivalent widths. This has already produced very important results and should also produce, in the future, information of ever increasing value as clearer and better knowledge of these absorption lines is obtained.

Most of this work has been carried out on the Fraunhofer lines in the solar spectrum because there the intensity is very much greater than in the stars. It is important, however, that corresponding studies be undertaken on stellar spectra. Prof. H. H. Plaskett, of the University Observatory, Oxford, was kind enough to place at the author's disposal some spectrograms of the star α-Lyrae which he had taken at the Dominion Observatory, Victoria, Canada. During the exposure of these plates a neutral tint wedge was placed over the slit of the spectrograph, and the variation in intensity so obtained could be used

as a means of calibrating the plate for photometric measurement. The present investigation was undertaken with the idea of measuring these plates and determining photometrically the profiles of the Balmer lines and of the stronger metallic lines in the spectrum; with these data it was hoped to test theoretical interpretations of the observed profiles with a vew to determining, among other things, the relative abundance of hydrogen to the metals on this star. Unfortunately, however, the author left Oxford before the latter part of the investigation could be completed, and the observational data are given in this paper that they may be used in future investigations.

In this paper the spectrograms have first been measured and the identity of as many of the lines as possible was determined. The profiles of the stronger lines were obtained and the total absorptions were measured from these profiles.

Wave-lengths and Identifications

Measurement of the Plates

The plates were measured on the Hilger measuring machine of the University Observatory, Oxford. Each spectrum was measured in the direct and reversed position, four different settings of the instrument being made for each measurement, and the mean of the two measurements was taken as the final reading for the line. The spectra were so broad that care had to be taken that no errors were introduced into the measurements by the curvature in the lines. Where possible all the lines were measured at the same position, but in some cases, owing to the variation in the intensity caused by the wedge, all the lines were not visible at the same wedge height, so that this procedure was impossible. Here the plates were measured in two sections, all the lines in each section being measured at the same height and the measurements from the two sections being then correlated so as to give one consistent set of readings, which was reduced as a whole. One plate (W445) was measured by Prof. H. H. Plaskett as well as by the author, in order to have one independent set of measurements which would eliminate the possibility of a personal error.

The reduction from millimetres to Angstrom units was carried out by means of a Hartmann formula, each set of measurements being reduced separately. By means of three stellar lines of which the identity was certain (Balmer lines were used where possible) the constants of the formula were determined for each plate, and, the wave-lengths having been calculated using these constants, most of the stronger metallic lines were easily identified. A number of these lines, chosen both for their intensity and sharpness in the spectra and for the absence of all possible blends, were then used to draw the curve of errors for the Hartmann formula, and from this curve the residual (O-C) was found for each individual wave-length. This residual was added to the wave-length computed by means of the formula, the result being the observed wave-length of the line. The standards used in these reductions are shown in Table I with an asterisk.

The mean of the wave-lengths computed from the plates (both values of the plate, which was measured twice, being used) is given as the final observed wave-length. In the reductions all wave-lengths were carried to the third decimal place, but in the mean value the third figure (and in some places the second) has been dropped as the accuracy did not warrant it. In measuring the plates all lines down to the absolute limit of visibility were measured, *i.e.*, everything on the plate that even remotely resembled a line, as it was assumed that lines due to spurious arrangements of silver grains would appear on only one plate. In the final list it was necessary to reject several as not representing actual stellar absorption lines. In rejecting these lines the following arbitrary criteria were used: All lines of wave-length shorter than 3800 Å were retained, as only one plate reached this region and it was impossible to distinguish between true and spurious lines. Between λ3800 and λ3900 Å all lines were rejected which were not registered on at least two plates, and above 3900 Å no line was retained unless it had been measured on three separate plates. In this way some real lines were almost certainly lost, but the loss of these lines is more than compensated for by the fact that there is little doubt that the lines finally retained are genuine.

Table of Wave-lengths

The wave-lengths finally determined are given in Table I. The second column contains the estimated intensity of the lines. These intensities are given in a purely arbitrary scale which has roughly the following value: The

TABLE I

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
3679.4	2	H_τ	79.36		10.16
3683.1	d 1	H_σ	82.81		10.16
*3685.1	1.5	Ti II	85.197	IV	0.605
3686.7	2	H_ρ	86.83		10.16
3691.3	2	H_π	91.56		10.16
3697.3	2.5	H_o	97.15		10.16
3703.8	2.5	H_ξ	03.86		10.16
3706.0	1.5	Ca II	06.02	V	3.110
		Ti II	06.22		
3709.2	0.3	Fe I	09.25	II	0.911
3711.8	d 5	H_ν	11.97		10.16
*3719.9	0.5	Fe I	19.938	I	0.000
3721.9	3.5	H_μ	21.94		10.16
3727.6	0.5	Fe I	27.62	II	0.954
3734.6	4	H_λ	34.37		10.16
3737.0	1	Ca II	36.90	V	3.137
		Fe I	37.14	I	0.051
3740.1	0.3				
*3741.8	1.5	Ti II	41.633	V	1.575
3743.4	0.4				
*3745.6	1	Fe I	45.56	I	0.087
		Fe I	45.90	I	0.121
3750.1	5	H_κ	50.15		10.16
*3758.2	d 0.5	Fe I	58.234	II	0.954
*3759.3	0.8	Ti II	59.294	IV	0.605
*3761.4	0.8	Ti II	61.322	IV	0.571

TABLE I—*Continued*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
3763.7	0.4	Fe I	63.79	II	0.986
3765.6	*d* 0.3	Fe I	65.54	IV	
3767.1	*d* 0.3	Fe I	67.19	II	1.007
3770.3	7	H$_\iota$	70.63		10.16
3783.3	0.3				
3797.9	8	H$_\theta$	97.90		10.16
*3815.93	0.5	Fe I	15.844	II	1.478
3820.42	0.7	Fe I	20.43	II	0.855
3824.40	0.4	Fe I	24.44	I A	0.000
*3825.88	0.7	Fe I	25.886	II	0.911
3827.77	0.4	Fe I	27.83	II	1.551
*3829.33	0.7	Mg I	29.36	II	2.697
*3832.29	0.7	Mg I	32.31	II	2.700
3835.40	8	H$_\eta$	35.39		10.16
*3838.29	0.9	Mg I	38.29	II	2.705
3843.31	0.3	Fe I	43.26	IV	
3849.93	0.3	Fe I	49.97	II	1.007
3853.63	0.3	Si II	53.68		6.827
3856.09	1	Si II	56.022		6.829
		Fe I	56.37	I A	0.051
3858.10	0.3				
3859.95	0.8	Fe I	59.91	I	0.000
3862.62	1	Si II	62.60		6.827
3865.56	0.4	Cr II	65.65		
		Fe I	65.53	II	1.007
3872.54	0.3	Fe I	72.51	II	0.986
3878.48	0.3	Fe I	78.02	II	0.954
		Fe I	78.58	II	0.087
		Fe I	78.66		2.443
*3889.05	10	H$_\zeta$	89.052		10.16
3900.60	1	Ti II	00.54	V	1.126
3902.99	0.4	Fe I	02.95	II	1.551
3905.60	0.6	Si I	05.53		1.900
		Cr II	05.66		
*3913.47	1.1	Ti II	13.460	V	1.111
3920.55	0.3	Fe I	20.26	I	0.121
3922.84	0.4	Fe I	22.92	I	0.051
3927.94	0.3	Fe I	27.92	I	0.110
3930.30	0.5	Fe I	30.30	I	0.087
3931.97	0.3	Ti II	32.01		1.126
*3933.67	8	Ca II	33.664	II	0.000
3943.98	0.8	Al I	44.03		0.000
3956.53	0.3	Fe I	56.46	IV	
		Fe I	56.68	III	2.681
3961.51	0.5	Al I	61.54		0.014
*3968.46	5	Ca II	68.470	II	0.000
*3970.08	7	H$_\epsilon$	70.075		10.16
4005.29	0.4	Fe I	05.25	II	1.551
*4012.38	0.6	Ti II	12.37	V	0.571
		Cr II	12.52		
4024.61	0.4				
4028.38	0.4	Ti II	28.33	V	1.884
*4045.81	1.8	Fe I	45.822	II	1.478
4053.90	0.4	Ti II	53.81	V	1.885
*4063.58	1.1	Fe I	63.604	II	1.551
4067.00	0.3	Fe I	66.98	III	
		Fe I	67.28	III	
*4071.74	0.9	Fe I	71.748	II	1.601
*4077.71	0.9	Sr II	77.71	II	0.000
*4101.74	10	H$_\delta$	01.738		10.16
4122.71	0.3	Fe II	22.67		2.572

TABLE I—*Continued*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
*4128.04	1.0	Si II	28.051		9.794
*4130.85	0.9	Si II	30.876		9.796
4131.98	0.4	Fe I	32.06	II	1.601
4143.82	0.7	Fe I	43.42	III	.
		Fe I	43.87	I	1.551
*4163.64	0.8	Ti II	63.647	V	2.579
4167.30	0.4	Mg I	67.39	III	4.327
*4171.90	0.6	Ti II	71.904	V	2.586
4173.44	1.0	Ti II	73.54	V	1.079
		Fe II	73.47		2.572
4177.70	0.4				
*4178.84	0.9	Fe II	78.868		2.572
4181.78	0.3	Fe I	81.76	III	
4187.16	d 0.3	Fe I	87.05	III	2.439
4198.95	d 0.4	Fe I	98.31	III	2.389
		Fe I	99.10	III	
4202.08	0.6	Fe I	02.03	I	1.478
4215.48	0.6	Sr II	15.52	II	0.000
4226.73	0.9	Ca I	26.73	I	0.000
4233.17	1.6	Fe II	33.16		2.572
4235.97	d 0.4	Fe I	35.95	III	2.415
4242.31	0.6	Cr II	42.35		3.854
4246.80	0.7	Sc II	46.83	III	0.314
†⎰4250.10	0.4	Fe I	50.13	III	2.458
⎱4250.83	0.4	Fe I	50.79	II	1.551
4254.38	0.4	Cr I	54.34	II	0.000
4258.21	0.3	Fe II	58.16		2.693
4260.43	0.7	Fe I	60.49	III	2.389
4262.00	0.4	Cr II	61.90		3.848
4271.75	0.8	Fe I	71.17	III	2.439
		Fe I	71.76	II	1.478
4273.26	0.4	Fe II	73.31		2.693
4290.17	0.8	Ti II	90.22	V	1.160
4291.77	0.3				
4294.09	1	Ti II	94.10	V	1.079
		Fe I	94.13	II	1.478
4296.56	0.6	Fe II	96.56		2.693
*4300.06	1	Ti II	00.052	V	1.175
4301.89 ·	0.4	Ti II	01.93	V	1.156
4303.17	0.7	Fe II	03.18		2.693
4307.87	1.2	Ti II	07.86	V	1.160
		Fe I	07.91	II	1.551
4312.82	d 0.4	Ti II	12.87	V	1.175
4314.96	0.6	Ti II	14.98	V	1.156
		Fe I	15.09	III	2.188
4320.81	0.4	Sc II	20.73	III	0.603
		Ti II	20.96	V	1.160
*4325.74	0.9	Fe I	25.770	II	1.601
*4340.47	10	Hγ	40.466		10.16
4351.79	1.2	Fe II	51.77		2.693
		Mg I	51.91	IV	4.327
*4383.55	0.9	Fe I	83.548	II	1.478
4385.29	0.6	Fe II	85.39		2.766
4390.64	0.5	Mg II	90.58		9.956
*4395.01	1	Ti II	95.036	V	1.079
4399.82	d 0.5	Ti II	99.77	V	1.232
*4404.74	0.9	Fe I	04.752	II	1.551
4415.14	d 0.4	Fe I	15.13	II	1.601
4416.94	d 0.4	Fe II	16.81		2.766
*4443.83	1	Ti II	43.799	V	1.075

†*Separable only on two plates.*

TABLE I—*Concluded*

Stellar λ, Å	Estimated intensity	Element	Lab. wave-length	Temperature class	E.P., volts
4466.73	0.4	Fe I	66.56	II	$\left\{\begin{array}{l} 2.819 \\ 3.005 \\ 0.110 \end{array}\right.$
		Fe I	66.94		3.912
*4468.50	0.9	Ti II	68.493	V	1.126
4471.50	d 0.4	He I	71.48		20.87
*4481.22	4	Mg II	81.327 } 81.129 }		8.825 } 8.826 }
4489.06	0.4	Fe II	89.21		2.816
4491.37	0.4	Fe II	91.41		2.843
*4501.28	0.7	Ti II	01.269	V	1.111
4505.27	0.2				
*4508.27	0.8	Fe II	08.287		2.843
*4515.35	0.8	Fe II	15.337		2.832
*4520.26	0.6	Fe II	20.238		2.795
*4522.71	0.9	Fe II	22.636		2.832
*4533.96	1	Ti II	33.966	V	1.232
4549.55	1.6	Ti II	49.62	V	1.577
		Fe II	49.48		2.816
4555.87	0.6	Fe II	55.90		2.816
4558.57	0.7	Cr II	58.66		4.056
4563.69	0.7	Ti II	63.76	V	1.216
4571.98	0.8	Ti II	71.97	V	1.565
4576.29	0.4	Fe II	76.31		2.832
4580.35	0.3				
*4583.84	0.9	Fe II	83.843		2.795
4588.21	0.6	Cr II	88.20		4.054
4618.81	0.4	Cr II	18.84		4.057
*4629.34	0.6	Fe II	29.327		2.795
4634.14	0.3	Cr II	34.12		4.055
*4861.31	10	Hβ	61.327		10.16
*4924.01	0.7	Fe II	23.92		2.879
4957.59	0.3	Fe I	57.61	III	2.796
		Fe I	57.31	III	2.839
*5018.43	0.8	Fe II	18.437		2.879

References to Wave-length Table

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*Si II.   King, A. S.   Astron. Soc. Pac. 38 : 324.   1926.   Jackson, C. V.   M.N.R.A.S. 94 :
     723-726.   1934.*

Sr II.   Fowler, A.   Report on series in line spectra.   Fleetway Press Ltd., London.   1922.

*Ti II.   Crew, H.   Astrophys. J. 60 : 108-121.   1924.   Russell, H. N. Astrophys. J. 66 : 283-328.
     1927.*

strongest hydrogen lines have intensity 10; a line which is easily and distinctly visible has intensity 1.0, while a line which can be distinguished only with difficulty has an intensity of 0.3. An intensity with a "*d*" in front of it signifies a very broad and diffuse line. The values given in the table are mean values from all the plates. The identification of the line is given in the third column, while the fourth column contains the laboratory wave-length. The fifth and sixth columns give the temperature class and excitation potential respectively of the lines. These were taken from Miss Charlotte E. Moore's "Multiplet Table of Astrophysical Interest". If the term values are desired they can easily be found in Miss Moore's "Term Designations for Excitation Potentials".

All together 156 lines were found in the spectrum, and of these 147 have been identified. The following are the elements which are present:

Hydrogen. The Balmer series was measured from H$_\beta$ to H$_\tau$ inclusive. These are by far the strongest lines in the spectrum, which is natural for a star of spectral class A$_0$. The later members of the series are all broad diffuse lines with distinct wings, so that it was impossible to measure them accurately; the measured wave-length for some lines differs considerably from the laboratory value, but they are so strong that there can be no doubt about their identification.

Helium. This is represented by the single line λ4471.48. One would expect to find λ3888, but this is undoubtedly masked by H$_\zeta$.

Magnesium I. The diffuse triplet λ3829, 3832, and 3838 is most certainly present. λ4351 is probably also present although blended with an Fe II line. The identification of λ4167 is very doubtful as there is no sign of λ4703.

Magnesium II. This is represented by the strong doublet λ4481 which is not separable. The line λ4390 is also present.

Aluminium I. The doublet λ3944, 3961 is definitely present.

Aluminium II. Does not seem to be represented. There is a stellar line at λ3900 which coincides with a strong Al II line, but the stellar intensity is such that the observed line can be completely accounted for by the Ti II line λ3900.54.

Silicon I. Almost certainly represented by λ3905 which is the only strong Si I line in this region.

Silicon II. Represented by five lines; the doublet at λ4128, 4131 and the three lines λ3853, 3856, and 3862.

Calcium I. The strong singlet λ4227 is certainly present, but the diffuse triplets which might be expected are absent.

Calcium II. The H and K lines are the strongest lines in the spectrum with the exception of the Balmer series. The doublet at λ3706, 3737 is also present, but the intensities in the star are anomalous. The short wave component is too strong, presumably owing to a blend with an unidentified line.

Scandium I.   The absence of λ3911, 4023 is conclusive evidence that Sc I is not present in the star.

Scandium II.   This is represented by λ4246 and rather doubtfully by λ4321.

Titanium I.   None of the strong lines of Ti I appear in the star.

Titanium II.   About 31 lines can safely be attributed to Ti II.   The stellar intensities are not in very good agreement with Russell's laboratory intensities, but the members of the same multiplets seem to be strengthened in the star, *i.e.*, multiplets 36 and 42.

Chromium I.   A weak stellar line at λ4254 coincides with the strongest Cr I line.   As this line is just visible and all other Cr I lines in this region are considerably fainter, it is not surprising that no other Cr I lines were found.

Chromium II.   Represented by nine lines all of which are fairly weak.

Manganese I.   There is no sign of the strong lines at λ4030 and 4033. Hence, Mn I cannot be present.

Manganese II.   Definitely not represented.

Iron I.   Between 50 and 60 lines are due to Fe I.   All the neutral iron lines in Burn's list with an intensity greater than six are present.

Iron II.   Represented by 24 lines.

Strontium I.   Not present.

Strontium II.   The resonance lines λ4077 and 4215 are definitely present.

The following unidentified lines were also found: 3740.1; 3743.4; 3783.3; 3858.10; 4024.61; 4177.70; 4291.77; 4505.27; 4580.35 Å.

Observed Profiles of the Balmer Lines

Determination of Line Profiles

The determination of the profile of an absorption line (*i.e.*, the distribution of intensity within the line) is the problem of translating a darkening of the photographic plate into an intensity of radiation incident on the plate.   In other words, the "characteristic curve" of the photographic plate, corresponding to the wave-length in question, must be known.   There are several methods of calibrating a photographic plate for such a photometric measurement, but in this investigation the calibration was obtained by the use of a neutral tint wedge.   This wedge was placed in front of the slit of the spectrograph during the exposure of the plate, and in this way a variation of intensity perpendicular to the spectrum was registered at all wave-lengths.   Since this variation of intensity is known from the constants of the wedge, it gives a means of relating the darkening of the plate with the intensity of incident light. This photometric method has been fully explained by Prof. H. H. Plaskett (7).

The amount of radiation absorbed must be known to determine the profile of an absorption line.   In other words, the ratio of the intensity at any wave-

length in the line to the intensity that would have been present at that wave-length if no absorbing matter were present has to be found. This latter intensity is generally referred to as the background intensity. Let I_o be the incident radiation, I_λ the radiation at λ in the line, and I_c the background radiation. Then r can be determined from

$$r = \frac{I_\lambda}{I_c} = \frac{I_\lambda/I_o}{I_c/I_o}$$

A determination of r together with the corresponding distance $\Delta\lambda$ from the centre of the line enables us to plot the observed profile.

The photometric measurement of these plates was carried out by means of the recording micro-photometer of the University Observatory, Oxford. A description of this instrument together with an exhaustive estimate of its performance has been given elsewhere (9). Tracings were taken of each line on each plate with this instrument, and tracings were also taken across the spectrum in the wings of each line in order to register the variation of intensity due to the wedge. On some plates two or more tracings were taken of the same line; since these were at different heights in the spectrum and, in consequence, had different intensities (and in effect, therefore, were separate exposures of the same duration), these tracings were equivalent to different plates and have been treated as such in this work.

An example of a tracing taken across H_β is shown in Fig. 1. A mean curve was drawn through the plate grain deflections, and a line through the continuous background was also drawn. In H_β it was necessary to draw the background with a slight curvature in order to obtain a smooth junction with the wings, but in some lines the background could be drawn perfectly straight across the line. Two tracings, one taken across the line and the other parallel to the line, are sufficient, when combined with a knowledge of the wedge constants, to delineate the profile. The procedure has been so clearly explained elsewhere (7, 8) that it is unnecessary to repeat it here. It is sufficient to say that the ratio I_λ/I_o for each point on the line and also the ratio I_c/I_o for the corresponding
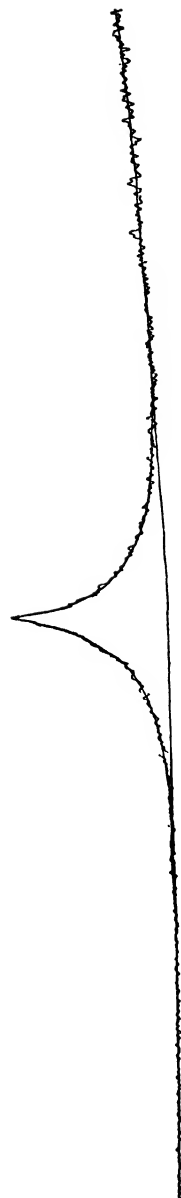
Fig. 1. *Microphotometer tracing of H_β.*

point on the background can be obtained.   The ratio of these two then gives *r*.

The distance of each point from the centre of the line is easily obtained in terms of the grid registered on the tracing. The magnification ratio of tracing to plate travel being accurately known from the microphotometer, these measurements can be converted to millimetre distances on the plate.   The problem is now reduced to translating these linear distances to Angstrom units, and this is the identical problem which was solved in the original measurement of the wave-length of the lines, so that the same procedure can be adopted, and the same constants for the Hartmann formula can be used.   The curve of errors obtained from the original measurements can also be used, and when the wave-lengths are corrected in this manner they are accurate to at least 0.1 Å.   It is necessary to go to this length in determining the wave-lengths in the profile because of the great width of some of the Balmer lines, which extend as far as 40 Å on either side of the centre.   If linear dispersion had been assumed across the line, a marked distortion in the width of the blue and the red wings would have been introduced.   When *r* and the corresponding wave-length for each point on the line had been determined, the profile of the line could be plotted.

Description of the Profiles

The profiles of the Balmer lines from H_β to H_ι inclusive and the K line of ionized calcium, determined by the above method, are reproduced in Figs. 2 to 9.   The measurements from all the plates are shown, and the agreement
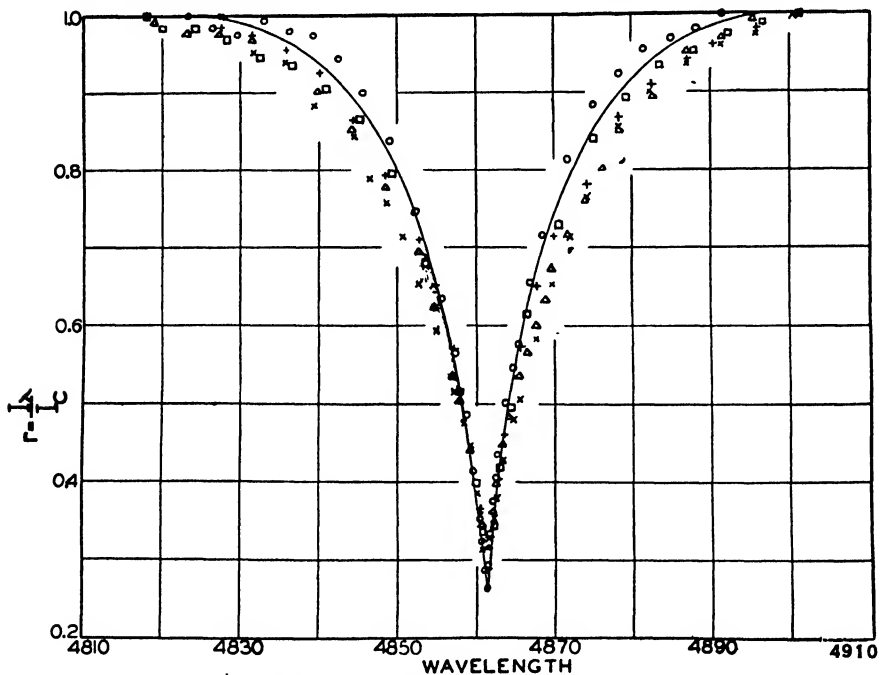
FIG. 2.   *Profile of H_β.*   O, *Plate 458a;* □, *Plate 458b;* ×, *Plate 443;* △, *Plate 459;* +, *Plate 445.*
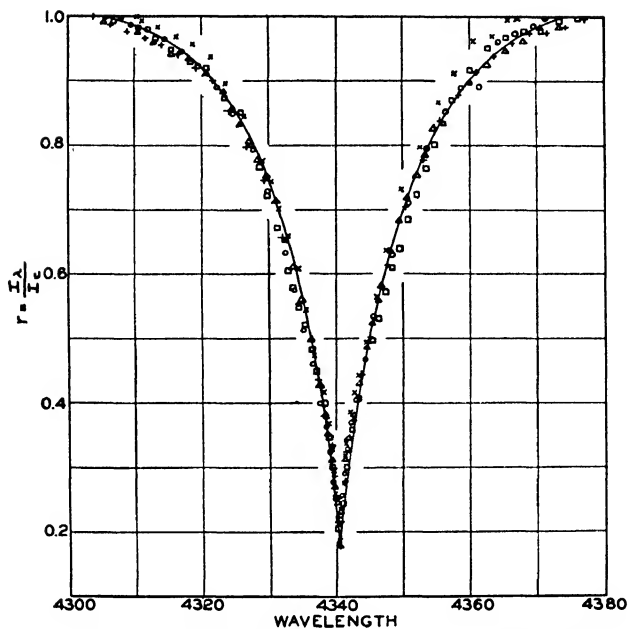
FIG. 3. *Profile of H*γ, ◯, *Plate 458;* ✕, *Plate 443;* △, *Plate 459a;* +, *Plate 445;* □, *Plate 459b.*
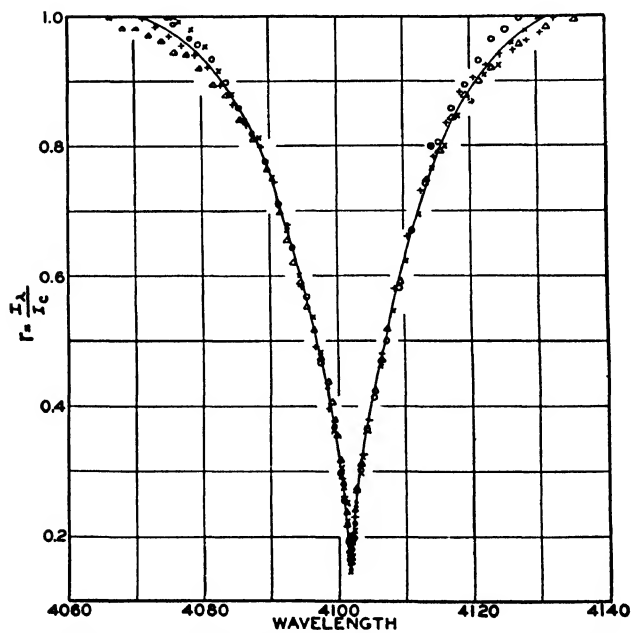
FIG. 4. *Profile of H*δ. ◯, *Plate 458;* ✕, *Plate 443;* △, *Plate 459;* +, *Plate 445.*
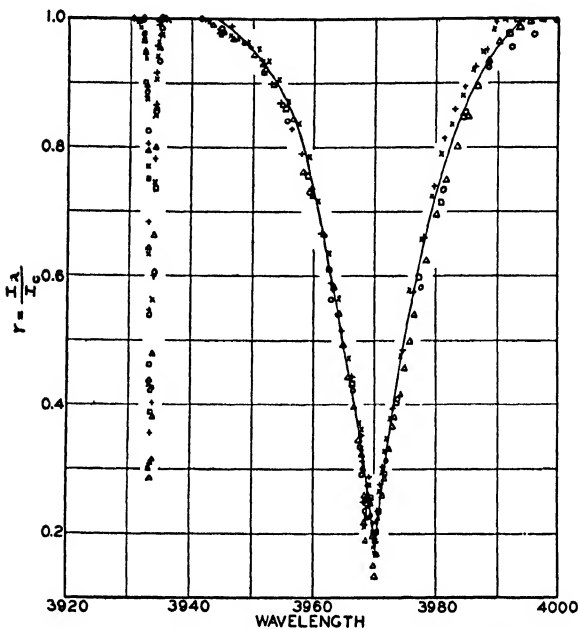
FIG. 5.   *Profile of* H_ϵ. $\bigcirc$, *Plate 478;* $\times$, *Plate 443;* $\triangle$, *Plate 459;* $+$, *Plate 445;* $\square$, *Plate 447.*
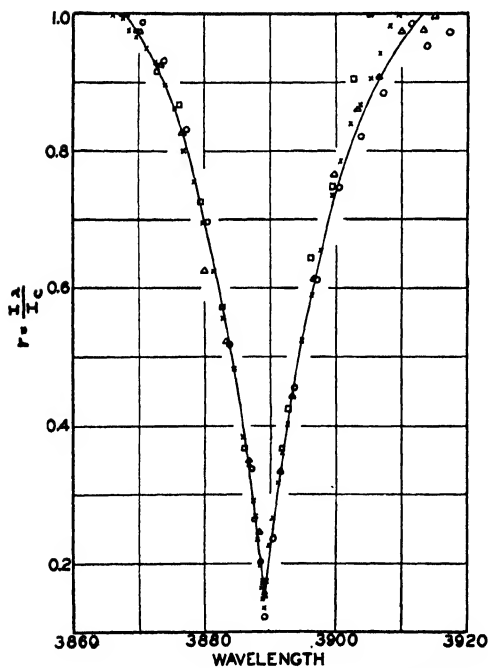
FIG. 6.   *Profile of* H_ζ. $\times$, *Plate 443;* $\square$, *Plate 447;* $\bigcirc$, *Plate 448;* $\triangle$, *Plate 447a.*
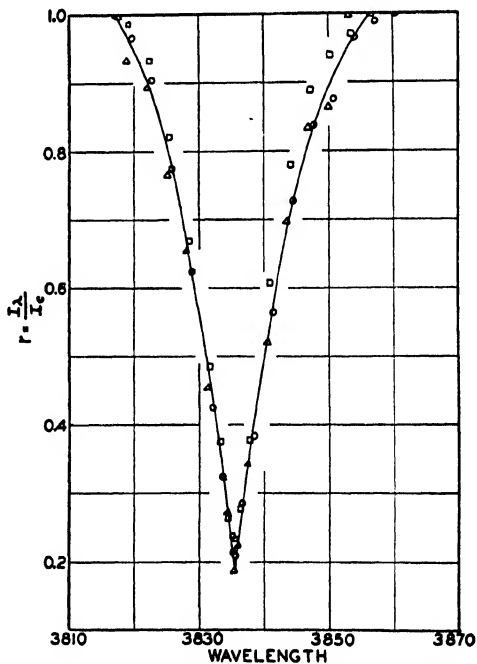
FIG. 7. *Profile of* H_η. $\square$, *Plate 447a;* $\triangle$, *Plate 447b;* $\bigcirc$, *Plate 448.*
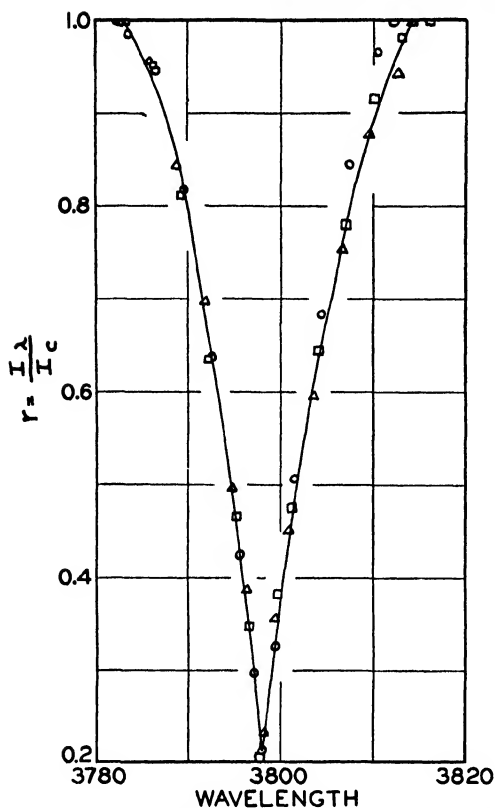
FIG. 8. *Profile of* H_θ. □, *Plate 447a;* △, *Plate 447b;* ○, *Plate 448.*
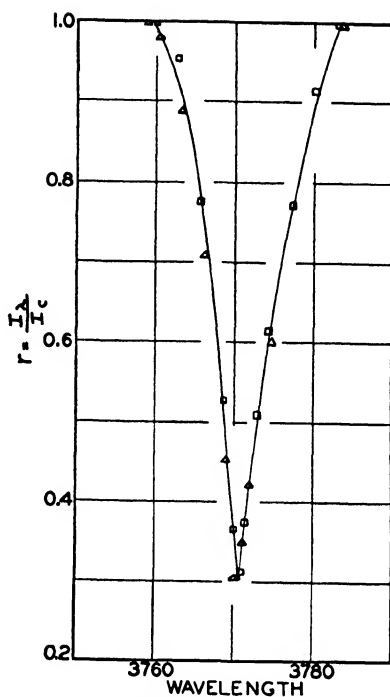
FIG. 9. *Profile of* H_ι. □, *Plate 447a ;* △, *Plate 447b.*

between the different sets of measurements is very striking. There is very little scatter in the readings except in the extreme wings of the lines where an exact agreement is hardly to be expected, since in this region a very small error in the position of the background would be very pronounced. The most unsatisfactory of all the profiles is that due to H_β, where a large difference in the profiles determined from the different plates even in the core of the line is found. It was obvious that there must be some reason for the fact that this line was so much less satisfactory than the others, and an examination of the focus test plates immediately showed where the trouble lay. Of the four plates only one, 458, was in focus at H_β, although all were quite satisfactory for the rest of the spectrum. A second tracing taken from this plate was then measured and good agreement with the first tracing was found except for some small scatter in the wing. A mean profile given by the two tracings from 458 has been used for all measurements, although the readings from all the plates are reproduced in the figure.

That this lack of focus on the plates should show up in the profile for H_β is a strong recommendation for the resolving power of the photometric method. The agreement of the profiles of the other lines is a further proof of this.

In each of the figures a mean profile has been drawn, and in Table II the values for r and the corresponding $\Delta\lambda$ are given for points on the profiles. The H line of ionized calcium appears in the violet wing of H_ϵ, but since this line is very narrow and not accurately delineated it has not been included in the mean profile.

TABLE II

MEAN LINE PROFILES

Line	$r = \dfrac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å	Line	$r = \dfrac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å
H_β	1.00	33.2	35.0	H_γ	1.00	35.0	33.6
	.98	28.0	28.1		.98	29.9	28.5
	.95	22.5	22.8		.95	24.4	23.9
	.90	17.1	17.3		.90	18.5	19.2
	.85	13.9	13.7		.85	15.4	15.8
	.80	11.4	11.1		.80	13.1	13.6
	.70	8.1	7.5		.70	9.3	10.0
	.60	5.0	4.8		.60	6.6	7.3
	.50	2.9	2.7		.50	4.4	4.6
	.40	1.2	1.3		.40	2.3	2.6
	.30	0.2	0.5		.30	0.8	1.1
	.262	0.0	0.0		.20	0.2	0.2
					.18	0.0	0.0
H_δ	1.00	30.9	30.5	H_ϵ	1.00	26.5	23.7
	.98	26.9	27.6		.98	23.9	21.6
	.95	23.0	24.1		.95	20.0	19.1
	.90	18.9	29.3		.90	16.1	16.0
	.85	16.0	16.2		.85	13.9	14.0
	.80	13.7	13.9		.80	12.1	12.2
	.70	10.1	10.3		.75	10.8	10.9
	.60	7.6	7.7		.70	9.5	9.5
	.50	5.1	5.3		.60	7.1	7.0
	.40	3.0	3.1		.50	5.1	4.9
	.30	1.6	1.4		.40	3.2	3.0
	.20	0.2	0.2		.30	1.5	1.7
	.16	0.0	0.0		.20	0.2	0.2
					.17	0.0	0.0
H_ζ	1.00	21.1	23.8	H_η	1.00	18.2	20.5
	.98	19.6	21.4		.98	17.0	19.3
	.95	17.7	20.0		.95	15.5	17.2
	.90	15.0	17.1		.90	13.3	14.6
	.85	13.0	15.0		.85	11.6	12.5
	.80	11.6	13.0		.80	10.4	10.7
	.70	9.1	10.0		.70	8.1	8.2
	.60	7.1	7.4		.60	6.3	6.2
	.50	5.2	5.4		.50	4.5	4.5
	.40	3.6	3.7		.40	2.9	2.9
	.30	1.9	2.0		.30	1.5	1.3
	.20	0.7	0.6		.20	0.1	0.1
	.13	0.0	0.0		.188	0.0	0.0
H_θ	1.00	14.9	16.1	H_ι	1.00	11.0	12.3
	.95	12.0	13.9		.95	8.7	10.7
	.90	10.2	12.1		.90	7.0	9.3
	.85	9.0	10.9		.85	5.9	8.2
	.80	8.1	9.5		.80	5.2	7.0
	.70	6.5	7.2		.70	4.2	5.2
	.60	5.0	5.2		.60	3.0	3.3
	.50	3.2	3.6		.50	2.2	2.1
	.40	1.9	2.2		.40	1.1	1.0
	.30	0.9	1.0		.30	0.1	0.1
	.207	0.0	0.0		.282	0.0	0.0

TABLE II—*Concluded*

MEAN LINE PROFILES—*Concluded*

Line	$r = \dfrac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å	Line	$r = \dfrac{I_\lambda}{I_c}$	$\Delta\lambda$ (violet wing), Å	$\Delta\lambda$ (red wing), Å
Ca II K-line							
	1.00	2.0	1.8		.70	0.4	0.5
	.98	1.4	1.4		.60	0.3	0.4
	.95	1.1	1.1		.50	0.2	0.3
	.90	0.7	0.8		.40	0.1	0.2
	.85	0.6	0.6		.30	0.05	0.05
	.80	0.6	0.6		.284	0.00	0.00

In much of the literature the intensity of a spectral line is expressed as a half-width, *i.e.*, the total width over which the absorption is greater than half the maximum. This value as determined above for the Balmer lines of α-Lyrae is given in Table III. The central intensity of the lines has also been included.

The half-width increases with the series up to H_δ, where a maximum occurs, and then it steadily decreases towards the series limit. A minimum value for the central intensity occurs at H_ζ. The fact remains, however, that there is great similarity, both with regard to shape and size, in the four lines H_γ, H_δ, H_ϵ, and H_ζ. The only pronounced difference is that the wings are slightly less extensive in the later members of the series. Beyond H_ζ the lines rapidly become narrower and less intense. This may be due to the overlapping of the wings of the lines, but an examination of the tracings did not seem to indicate such an overlapping for lines of wave-length shorter than H_θ. However, since other investigators have found this overlapping even as early as H_δ (4, p. 282), too much emphasis cannot be placed on the fact that the author's lines appear to become both shallower and narrower, as we proceed beyond H_ζ, as this might quite well be due to the overlapping. For lines of wave-length shorter than H_ζ, however, the author places full reliance on the profiles. There does not appear to be any indication of asymmetry in any of the lines.

TABLE III

Line	Half-width, Å	Central intensity, $r = \dfrac{I_\lambda}{I_c}$
H_β	11.6	0.26
H_γ	13.3	0.18
H_δ	14.1	0.16
H_ϵ	13.5	0.17
H_ζ	12.9	0.12
H_η	12.1	0.19
H_θ	10.3	0.21
H_ι	7.7	0.28

Total Absorptions

To obtain the total absorption (or equivalent width), $\int_{-\infty}^{+\infty}(1 - r)d\lambda$, of a line is a comparatively simple matter once the profile has been determined. It is most easily done by plotting $1 - r$ against λ and integrating the area under the curve with a planimeter. The total absorption, which has the dimensions

of a length, is usually expressed as Angstroms of continuous spectrum, and this method has been followed here. For profiles of the hydrogen lines and that of the calcium K-line, the mean value of r, as obtained from the curves, was used to plot $1 - r$, and the area under this mean curve was taken as the equivalent width. In the weaker metallic lines, however, the irregularities due to the plate grains were comparable in size to the absorption line itself; this made it extremely difficult to draw a mean profile. In this case it seemed preferable to plot $1 - r$ for each individual tracing, determine the corresponding equivalent width, and take the mean of these values for the total absorption. By taking a sufficient number of tracings the spurious effects due to the silver grains should be eliminated. This method differs from that used by Struve and Elvey (11, p. 416). They measured the base and central intensity of the line on the tracing and then computed the area by assuming the line to have a triangular contour.

In Table IV are given, not only those results obtained in this investigation, but also, for comparison purposes, the total absorptions from all previous investigations of the spectrum of α-Lyrae.

A study of this table shows that the results obtained in this investigation are not always in agreement with previous observations. The absorptions obtained by Elvey for H_β and H_γ are considerably larger than those obtained by the author. The other observers, however, give better agreement, and when the present determinations are compared with the mean of all the others as given in the last column, the agreement is fully as good as one might expect. The experimental conditions of the present investigation were such that the author feels justified in placing considerable reliance on the results even when they are at variance with other observations. The following considerations lead us to this conclusion:

(1) The large resolving power of the plates, coupled with the excellent performance of the microphotometer.

(2) The dispersion of the plates (23 Å per mm. at H_β; 10.92 Å per mm. at H_δ). It has been suggested by Minnaert (6, p. 329) that a large dispersion gives a greater total absorption than a small dispersion, and it seemed as if this might account for the fact that the total absorptions obtained by the author are larger than those of Elvey. There was, however, an opportunity to test this, as both one-prism and two-prism plates were available in the region $\lambda 3900$ to $\lambda 4000$. The hydrogen lines H_ϵ and H_ζ and the K-line of Ca II are in this region, and the fact that no difference in the profiles of these lines as determined from the one-prism and the two-prism plates was found seems to contradict Minnaert's observation, at least within the limits of the dispersion.

(3) Because of the nature of the plates it was possible to measure spectra with large variation in the blackening of the plate, but with identical exposure times. Hence, in effect, an infinite series of spectra of varying intensity are available, so that it is possible to measure the line profile at any intensity.

TABLE IV

No. of tracings	Line	Present investigation		Struve & Elvey (11, p. 418) (log A)	Elvey (2)	Gunther (5)	Williams (15)	Dunham (1)	Williams (16)	Elvey & Keenan (3, p. 224)	Mean of all measurements except the present
		$A = \int_{-\infty}^{+\infty}(1-r)d\lambda$	log A								
2	H$_\beta$	12.01	1.08		18.18	14.7	12.9			18.2	16.0
5	H$_\gamma$	14.37	1.16		21.18	15.1	15.58	13.9	18.1	21.2	17.5
4	H$_\delta$	14.98	1.18			16.6	12.92	13.4	16.19	14.9*	14.8
5	H$_\epsilon$	13.30	1.12			14.2		13.89			14.1
4	H$_\zeta$	13.45	1.13			13.5					13.5
3	H$_\eta$	11.33	1.05			13.4					13.4
3	H$_\theta$	9.15	0.96			9.8					9.8
2	H$_\iota$	6.12	0.79			6.5					6.5
5	Ca II (3933)	0.648	−0.19						0.93		0.93
9	Ca I (4227)	0.057	−1.24	−1.12							0.076
15	Mg II (4481)	0.293	−0.53	−0.29							0.513
4	Sr II (4215)	0.036	−1.44	−1.35							0.045
4	Sr II (4078)	0.046	−1.34								
4	Si II (4128)	0.062	−1.21								
4	Si II (4130)	0.060	−1.22								
4	Fe I (4063)	0.058	−1.24								
4	Fe I (4072)	0.041	−1.39								
4	Fe II (4179)	0.064	−1.19								
4	Fe II (4233)	0.061	−1.21	−0.91							

Single prism.

The fact that the profiles, as measured on the different plates and at different wedge heights, all agreed is fairly conclusive evidence of the reliability of the measurements. It seemed worth while also to make a detailed comparison of the total absorptions to determine if there was any variation with intensity. The results for the lines λ4481 Å of Mg and λ4227 Å of Ca are given in Tables

V and VI. The column headed "transmission in the continuous spectrum" gives the ratio of the light transmitted through the continuous spectrum at the wedge height in question to that transmitted through the unexposed plate, and thus gives an indication of the blackening of the plate.

TABLE V

λ4481Å

Plate 443		Plate 459		Plate 458		Plate 445	
Transmission in cont. spec.	A	Transmission in cont. spec.	A	Transmission in cont. spec.	A	Transmission in cont. spec.	A
0.420	0.272	0.282	0.258	0.360	0.339	0.324	0.346
0.345	0.250	0.254	0.328	0.268	0.278	0.310	0.359
0.292	0.232	0.140	0.292	0.126	0.284	0.106	0.270
0.234	0.248						
0.222	0.254						
0.189	0.266						
Mean	0.254		0.293		0.300		0.325

Mean of four plates: 0.293.

TABLE VI

λ4227 Å

Plate	Transmission in cont. spec.	A
443	0.444	0.049
459	0.342	0.050
443	0.318	0.066
458	0.246	0.069
443	0.233	0.068
443	0.225	0.066
443	0.186	0.035
445	0.185	0.066
443	0.160	0.045

There is no indication of any systematic change of total intensity with the blackening, and these measurements, combined with the fact that good agreement was found in the hydrogen profiles as determined at different heights, leads the author to assert that within certain limits the total absorption is independent of the blackening on the plate. With the line λ4481 Å, however, it is found that the readings from Plate 443 are considerably smaller than those from the other plates. This is difficult to account for. The plates were all equally well focused at this wave-length. None of the other lines seem to show this effect; this argues against instrumental errors. The fault could hardly lie in the calibration curve, as the readings from Plate 443 are consistent among themselves. It almost seems as if there must have been some intrinsic change in the absorption line at the time when Plate 443 was exposed, although it is difficult to account for such a variation in the intensity of a line. For the purpose of tabulation the mean of the four plates was taken, each plate being given equal weight.

(4) It is probable that a large part of the discrepancy between the results obtained by the different observers arises through the uncertainty in the position of the continuous background (4, 17). Elvey and Struve have shown that when they compute the total absorption of a line, using continuous
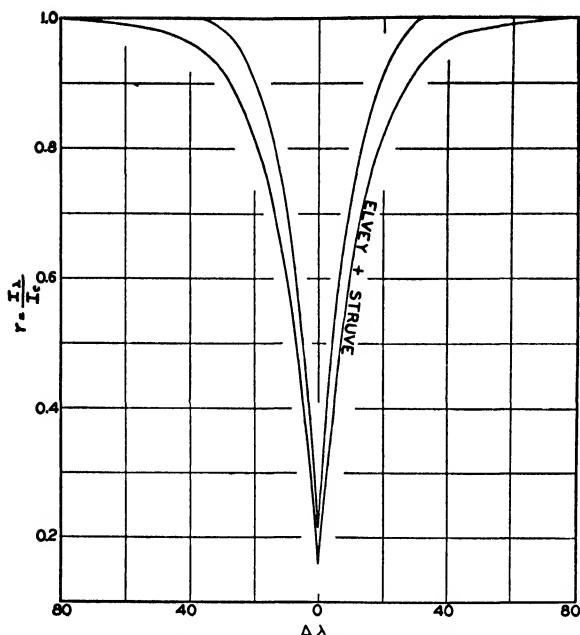
FIG. 10. *Comparison of the profile obtained for H$_\gamma$ by Elvey and Struve with that obtained in this investigation.*

backgrounds that differ by 1 mm. on their tracing, the results that they obtain differ by 18%. If the position of the background as it is drawn on their tracings is compared with the present tracings, it appears as if the background has been drawn consistently lower than theirs. In Fig. 10 is shown a comparison between the profile of H$_\gamma$ given by them (4, p. 283) with that obtained from Plate 458. It is immediately evident that their line is much wider. In order to see if this difference could be due to the position of the background, a determination was made of the position in which the background would have had to be drawn in order to make the present profile coincide with theirs. This background is shown as a broken line in Fig. 11. It is quite clear that it would be impossible to draw the background in this position. The position of the background, therefore, cannot account for all the difference between Elvey and Struve's profiles and those obtained in this investigation. A wider line and a larger total absorption could have been obtained by draw-
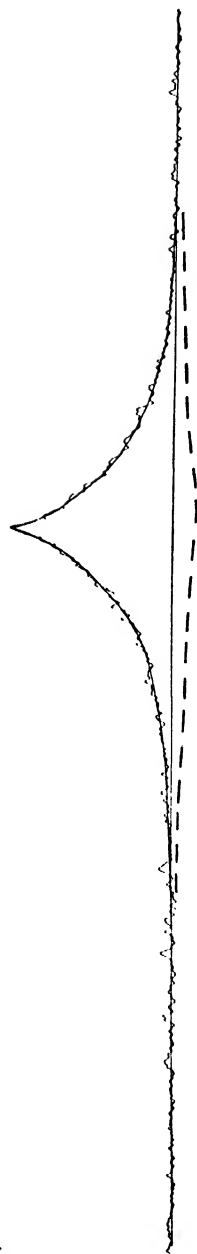
FIG. 11. *Microphotometer tracing of H$_\gamma$. The broken line shows how background must be drawn to make profile coincide with that of Elvey and Struve.*

ing the background higher, but there does not seem to be any justification for this. A study of tracings taken with smaller magnification shows that there is no reason for believing that the continuous background does not go straight across the line, and that once outside of the wings of the line the tracing does not register the background. Hence, the mean position of the plate grain deflections should give the continuous spectrum, and on this basis the background has been drawn.

Conclusion

The profiles of the Balmer lines which have been presented in this paper are available as a means of testing any theoretical formulas which may be advanced as an explanation of the formation of absorption lines in A_o stars. All the formulas which are at present available were tested during this investigation without any satisfactory results. Neither a natural radiation damping formula similar to that employed by Unsöld (12, 13, 14), nor the use of a Doppler absorption coefficient will produce a theoretical formula that agrees with the observed Balmer profiles. The most hopeful line of attack seems to be that given by Pannekoek and Verwey (10) in which they apply the Stark effect to the broadening of the hydrogen lines in early type stars. The theoretical lines which they obtained are very similar in shape to the author's observed Balmer lines, and a satisfactory explanation may be obtained in this way.

The total absorptions should lend themselves very easily to a determination of the relative abundance of the different elements in the star. A knowledge of the curve of growth connecting the observed total absorptions with the number of atoms is required. With this curve it would be possible to estimate directly the ratio of hydrogen to the metallic atoms in the star, a problem of great importance to Astrophysics. Other results will also follow, such as an estimate of the electron pressure and the temperature at the point at which the lines originate in the stellar atmosphere.

Acknowledgment

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ERRATUM

Page 354, second paragraph, line 13, for "100 cc." read "50 cc."

FORCE MEASUREMENTS ON STOP-LOG MODELS[1]

By K. F. TUPPER[2]

Abstract

A model of a stop-log emergency dam was built for the purpose of obtaining measurements of the hydrodynamic forces acting on the logs during placement. It is considered that the results are of interest to engineers faced with the design of similar structures. They are accordingly presented in non-dimensional form. The single restriction on the applicability of the results lies in the geometry of the structure where the vertical height of the log is exactly one-sixth the depth of the canal.

Logs of three cross sectional shapes were tested, namely, circular, square, and 2 : 1 rectangular (2 horizontal, 1 vertical). The forces were measured on each of the first four logs to be placed in the stream.

Introduction

Emergency dams are provided at the upper entrance to canal locks leading out of large bodies of water such as lakes. Their function is to shut off the flow of water, which would occur should the lock gates be destroyed by accident. The potential damage which would occur by flooding in the event of such an accident is often enormous, and the cost of an emergency provision for obstructing the flow is justified.

The stop-log type of dam consists of a set of logs of length slightly greater than the width of the canal whose ends fit in a groove or recess in the canal wall, and a special crane which can be swung across the canal and which picks up the logs by an attachment to each end. Heavy weights are carried by the crane immediately above the log and serve to force the log downwards through the water. The logs are constructed of structural steel and are made permeable so that they fill with water.

The design of the hoisting gear, and to a lesser extent that of the logs themselves, is contingent upon a knowledge of, or an assumption of, the forces both vertical and horizontal acting on the log during placement. The horizontal force will determine the friction force (vertical) of the log ends in the grooves as they are moved, and this, added to the vertical component of the hydrodynamic force, constitutes the force which the weights and the crane must be able to overcome in lowering and raising a log respectively.

An utter minimum of design data has been secured from the operation of full-scale structures, because to date no large-sized emergency dam has been

required to operate under emergency conditions. Obviously a suitable test condition, which means a free discharge through a short length of canal, cannot be obtained.

It might be mentioned in passing that to *guess* the magnitude of the hydro-dynamic forces is a matter of virtual impossibility. Indeed it is likely that even the sign of the vertical force will be wrong in a guess, and the magnitude may be seriously in error.

The present model tests, although the results may be affected by scale, and to a slight extent by inaccuracies of representation in the model, are believed to provide a useful guide to designers of stop-log emergency dams.

Description of the Apparatus

The apparatus was built for the investigation of a specific problem, and represents a 1/100 scale model of a portion of the Welland canal. Fig. 1 presents a schematic drawing of the equipment as a whole, with the principal
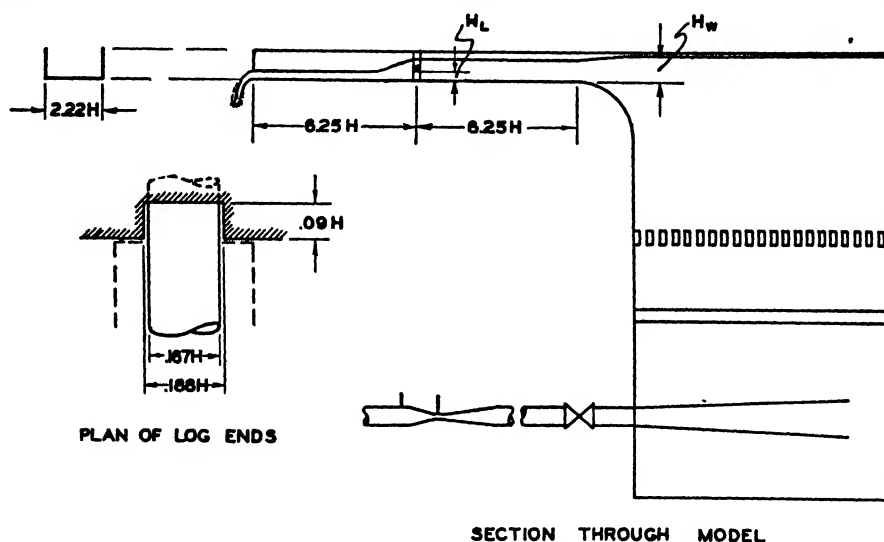
FIG. 1. *Sketch showing general layout of stilling basin and canal model.*

dimensions. Fig. 2 is a photograph of the canal model proper, with stop log and balance in place. Fig. 3 is a photograph of the balance assembly and model.

The water supply was obtained from the city mains through a 3 in. pipe line containing a Venturi meter and two gate valves. A stilling basin 6 ft. deep and 2.5 by 3.5 ft. in planform connected the pipe line to the model with a bell mouthed transition section. The stilling basin was fitted with a pair of slat racks and with an expansion cone on the inlet pipe.

The canal model was made of sheet brass and was 0.80 ft. wide and 0.36 ft. deep. The outlet end was fitted with a hinged plate which could be raised; this formed an adjustable weir crest. This was provided as a method of controlling the downstream water level, but was not used.

PLATE I
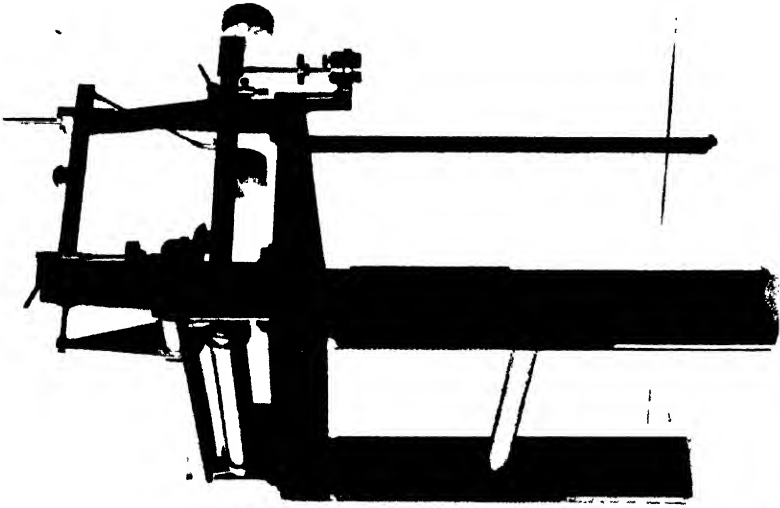
FIG. 3. View of balance, detached.
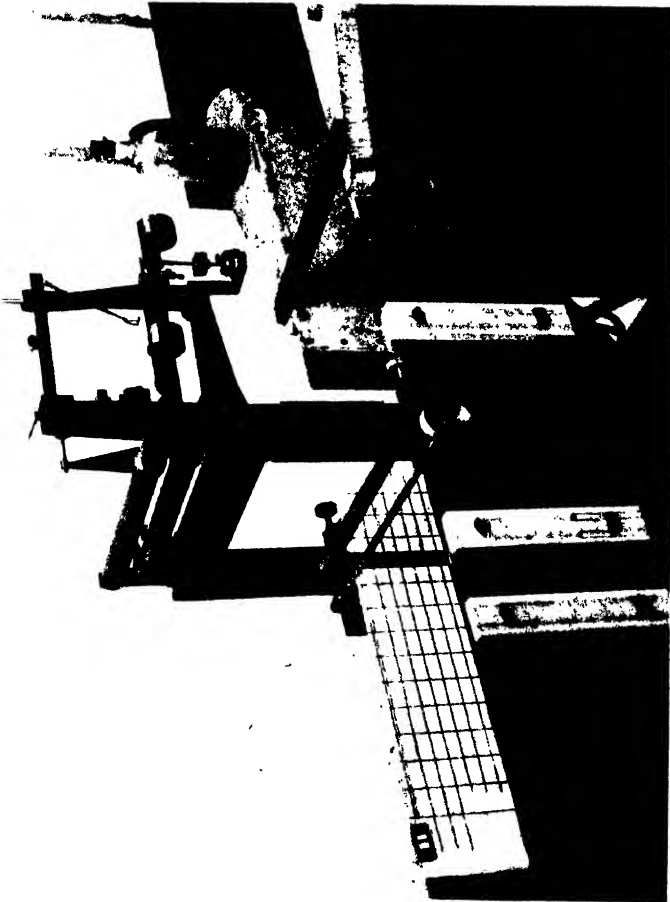
FIG. 2. View of canal model with balance and circular log in place (elevated).

The stop-log models were supported by a balance which was mounted on an inverted U-frame straddling the canal model. The balance was arranged to measure separately the horizontal and vertical components of the hydrodynamic force. The balance could be raised and lowered by a rack and pinion or clamped at any desired height. Fig. 4 is a schematic diagram of the balance mechanism.

A hook gauge was installed in an external chamber to measure the water level in the stilling basin, which constitutes the head of water acting on the model. A number of glass tube manometers were attached to the bottom of the canal model to provide a measurement of the depth of water at various points. The manometers are shown in Fig. 2.

LIFT

DRAG

DIAGRAMMATIC ARRANGEMENT OF BALANCE

FIG. 4

Operational Technique

Each series of tests was made with a constant discharge through the model, regulated by means of the valves in the supply pipe line and measured by means of the Venturi meter. This meant that the upstream (stilling basin) water level changed from its nominal value during each test according to the vertical
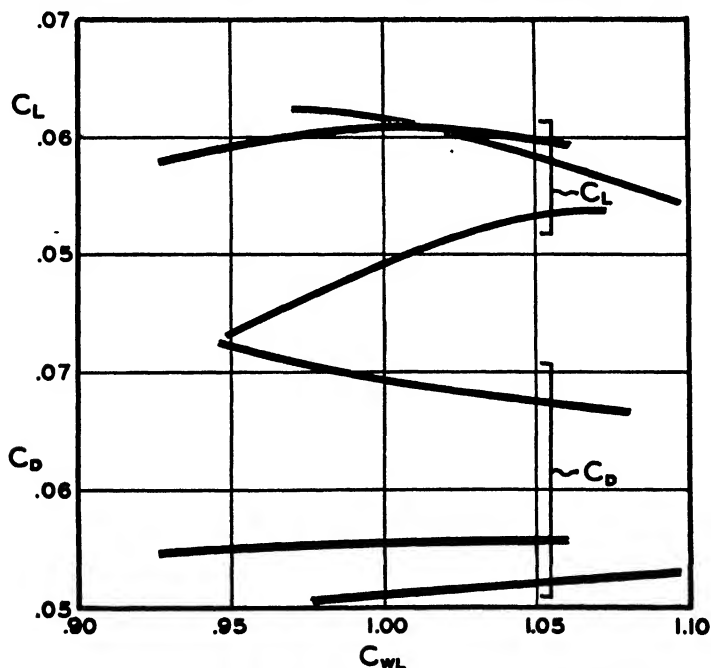
FIG. 5. *Results of tests showing influence of upstream water level upon model forces.*

position of the log. The discharge was so chosen as to give an average value of upstream water level that was approximately correct. This technique was chosen because of its simplicity.

To get an idea of the errors involved because of failure to maintain correct head and to have the correct discharge, a few tests were made with circular logs in the position giving the maximum force, a range of discharges being used. The results are presented in Fig. 5 and show that small variations from the correct discharge cause only negligible variations in the maximum force.

Non-dimensional Coefficients

The results of the force tests are presented in non-dimensional form. Strictly the results are applicable only to exactly similar cases, but because the flow is substantially two dimensional the error will be small for applications to the case in which the dam cross section is exactly similar and the canal width is equal to, or greater than, the depth.

Symbols Used

Dimensional Coefficients

Symbol	Definition	Dimensions
H	Depth of canal	Length
H_L	Height of log above bottom of canal	Length
H_W	Height of upstream water level above bottom of canal	Length
B	Breadth of canal	Length
Q	Discharge	Length³ Time⁻¹
L	Lift force (vertical)	Length Mass Time⁻²
D	Drag force (horizontal)	Length Mass Time⁻²
g	Acceleration of gravity	Length Time⁻²
ρ	Fluid density	Mass Length⁻³

Non-dimensional Coefficients

Symbol	Definition	Derivation
C_{LH}	Log height coefficient	$\dfrac{H_L}{H}$
C_{WL}	Water level coefficient	$\dfrac{H_W}{H}$
C_D	Drag coefficient	$\dfrac{D}{BH^2\rho g}$
C_L	Lift coefficient	$\dfrac{L}{BH^2\rho g}$
C_Q	Discharge coefficient	$\dfrac{Q}{BH^{1.5}g^{0.5}}$

Calculation of Full-scale Forces

Full-scale forces are calculated from the lift and drag coefficients in the following manner.

$$\text{Lift force, } L = C_L B H^2 \rho g$$
$$\text{Drag force, } D = C_D B H^2 \rho g.$$

It may be noted that the factor BH^2 has the dimensions of a volume, and is the scale multiplier; the factor ρg is the weight density of the water (or other fluid to which the experimental results could as well be applied).

Range of Variables Explored

1. Log Height Coefficient

The log height is defined as the vertical distance from the floor of the canal to the bottom of the log under consideration. The lower limit of C_{LH} for each of the first four logs is therefore 0, 0.167, 0.333, and 0.5 respectively. The upper limit of C_{LH} was determined by the flow condition prevailing, since ultimately on raising the log it came quite clear of the stream and experienced no hydrodynamic force. The first log usually came out of the water at C_{LH} about 0.67, and the next three logs each came out at C_{LH} about 0.75.

It should be noted that in gradually *raising* a log the highest value of C_{LH} for which the log is still partly immersed is greater than the value of C_{LH} at which the log first touches the stream when being *lowered*. In the latter case as soon as the log touches the stream a wave is created on the upstream side of the log, and it traverses slowly upstream, ultimately disappearing into the stilling basin. On changing the height of the log in either direction, the hydraulic conditions are transient for a considerable period of time, and it is impossible to make reproducible force measurements. As a consequence all measurements were made under steady conditions which might not be encountered in practice if a log is being moved at all quickly. It is considered that the general magnitude of the forces prevailing under transient conditions is the same as that of the steady forces which were measured; the behavior of the balances did not give any indication to the contrary.

2. Shapes of Log

Logs of three cross sectional shapes were tested, namely;—circular, square, and 2:1 rectangular, the last with its larger dimension horizontal. The shapes are shown in Fig. 6, assembled to form a complete section of a dam.
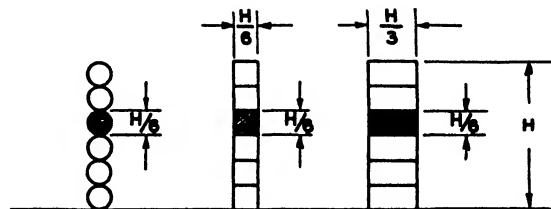
SHAPES OF LOGS AND DAMS

Fig. 6.

3. Discharge Coefficient

As explained above, the discharge, and hence the discharge coefficient, was maintained constant during the tests on each individual log. The discharge coefficients prevailing during the tests are given in Table I.

TABLE I

DISCHARGE COEFFICIENTS

Log	Circular	Square	Rectangular 2 : 1
1st	0.459	0.428	0.418
2nd	0.388	0.357	0.347
3rd	0.286	0.245	0.246
4th	0.173	0.135	0.136

Accuracy of Measurement

Drag

Repeated readings of drag usually agreed to about 1%, but in some cases they differed by as much as $2\frac{1}{2}$%. The drag force appeared to be fluctuating continuously. The measuring technique therefore consisted of an attempt to measure upper and lower limits, and then setting the balance at a reading midway between these and watching to ascertain whether the departures on each side were equally numerous. As a rule the measurement of drag presented no difficulty, the only exception being when a log was just emerging from the stream, and then conditions were quite unsteady.

The drag measurement is not exact owing to a deficiency of the balance used, wherein the pitching moment acts on the drag beam and influences the results. From previous unpublished tests of forces on cylinders of circular and square cross section under similar conditions, it was found that the resultant force never had an eccentricity greater than one-sixth the diameter of the cylinder. On the assumption that this is true also for the rectangular shape, the maximum error introduced on this account in the present tests would be $1\frac{1}{2}$%. The lift measurement is free from this complication.

Lift

The lift balance exhibited wide variations in stability owing directly to the variation in lift with variation in log height. In order to make lift measurements, the log must be free to move slightly in a vertical direction. This amounts to a minute change in log height, and, hence, depending on $\frac{dL}{dH_L}$, to a change in the vertical force. If the slope of the lift curve against log height, $\frac{dL}{dH_L}$, is negative, the balance is stabilized and hence insensitive, but if the slope is positive, the balance is unstable.

As a consequence of this phenomenon the measured lifts, when $\frac{dL}{dH_L}$ had large negative values, are subject to considerable error. This is the case when a log is in its lowest position, and all the lift measurements in this position are uncertain. When $\frac{dL}{dH_L}$ had a positive value the lift balance was unstable, and required to be operated in a special manner allowing only very small motions of the log. When this was done the readings were satisfactory.

Scale Effect

The temperature of the water during the experiments varied from 10° to 20° C. The corresponding kinematic viscosities are 1.4 and 1.1 × 10^{-5} ft.^{2} sec.$^{-1}$. The Reynolds number may be computed using as a length dimension the depth of the water. Let v be the mean velocity at a section, and d the depth. Then $vd = \dfrac{Q}{B}$ and the Reynolds number, Re $= \dfrac{vd}{\nu} = \dfrac{Q}{B\nu}$. In the present tests $\dfrac{Q}{B}$ ranged from 0.165 to 0.562 ft.^{2} sec.$^{-1}$, so that the corresponding Reynolds numbers fall in the region between 12,000 and 51,000.

It is believed that the general flow in the model was of a turbulent nature, and that scale effects would not be severe. There is a possibility that the flow past the circular logs might be in the "mixed flow" regime, and that the drag force measurements in particular might be low on that account.

Results

A. Force Measurements

The results of the force measurements are presented in graphical form in Figs. 7 to 12 inclusive as a plot of C_L or C_D against C_{LH}, and in Fig. 13 as a plot of C_L against C_D. The latter presentation constitutes a polar diagram, and a line drawn from the origin to any point on a curve will have the same direction as the resultant force corresponding to that point.

It is interesting to note that the forces are smallest for the circular shape and largest for the 2 : 1 rectangular. The vertical forces are particularly large for the 2 : 1 rectangular shape. The inclination of the resultant force varies from about +55° to −50°.

B. Flow over Partial Dam

The shape of the water profile is shown in the photographs assembled in Figs. 14 and 15. The grid of lines on the canal wall was intended for the specific case under investigation and represents 5- and 10-ft. intervals full-scale. In non-dimensional form the spacing of the horizontal and vertical
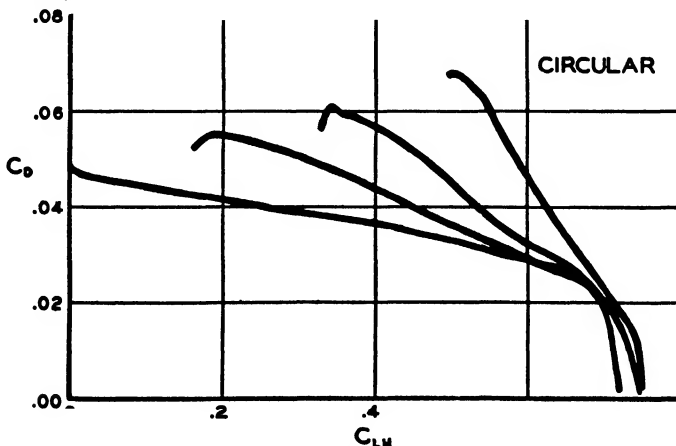
FIG. 7. *Results of force measurements.*
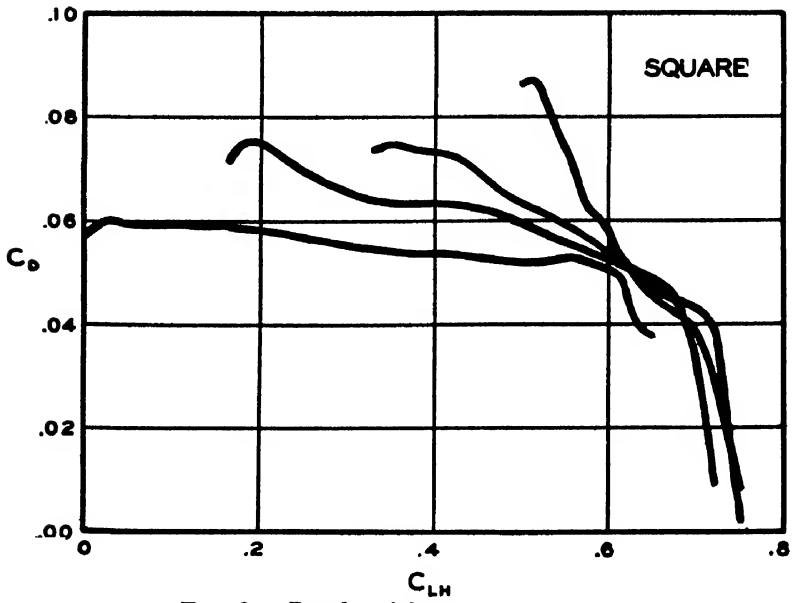
FIG. 8.   *Results of force measurements.*
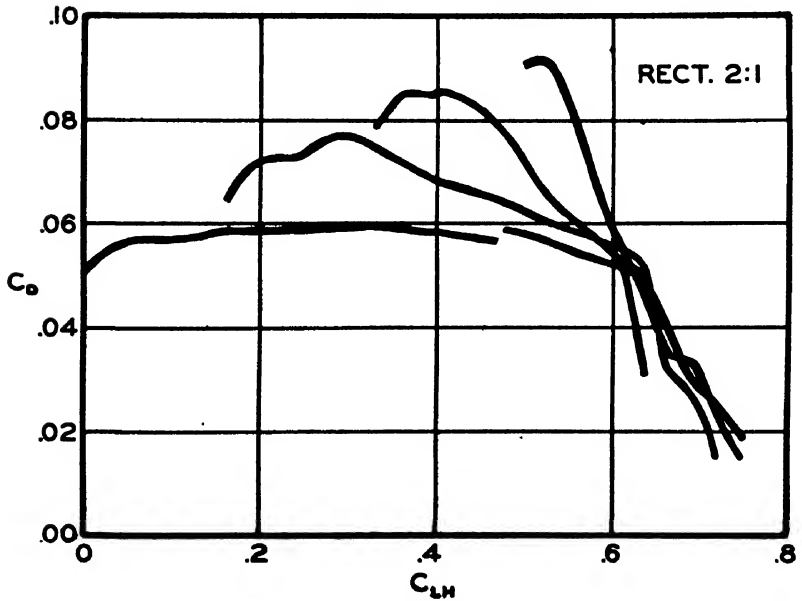
FIG. 9.   *Results of force measurements.*
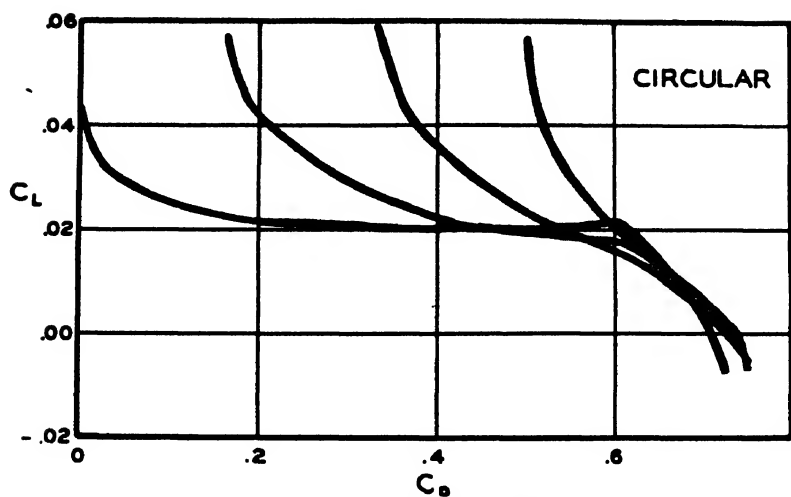
FIG. 10.   *Results of force measurements.*
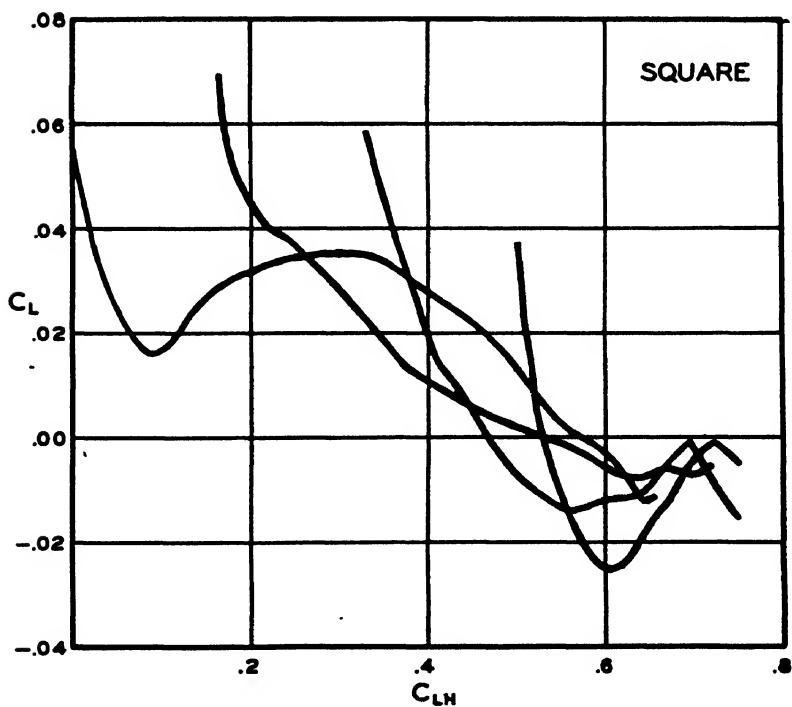
FIG. 11.   *Results of force measurements.*
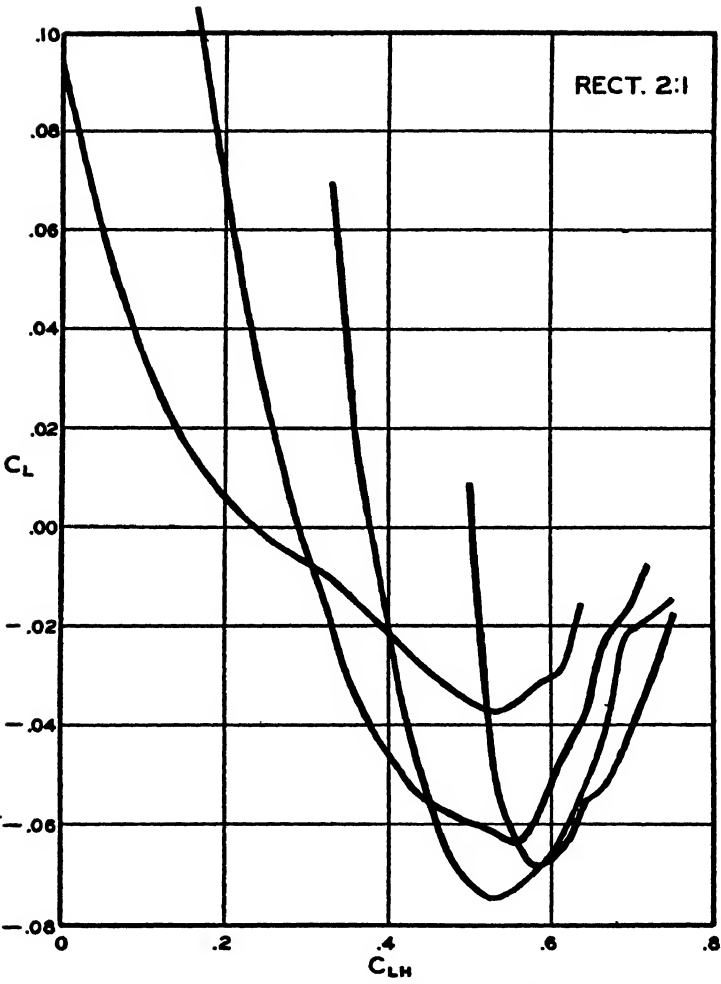
FIG. 12.   *Results of force measurements.*
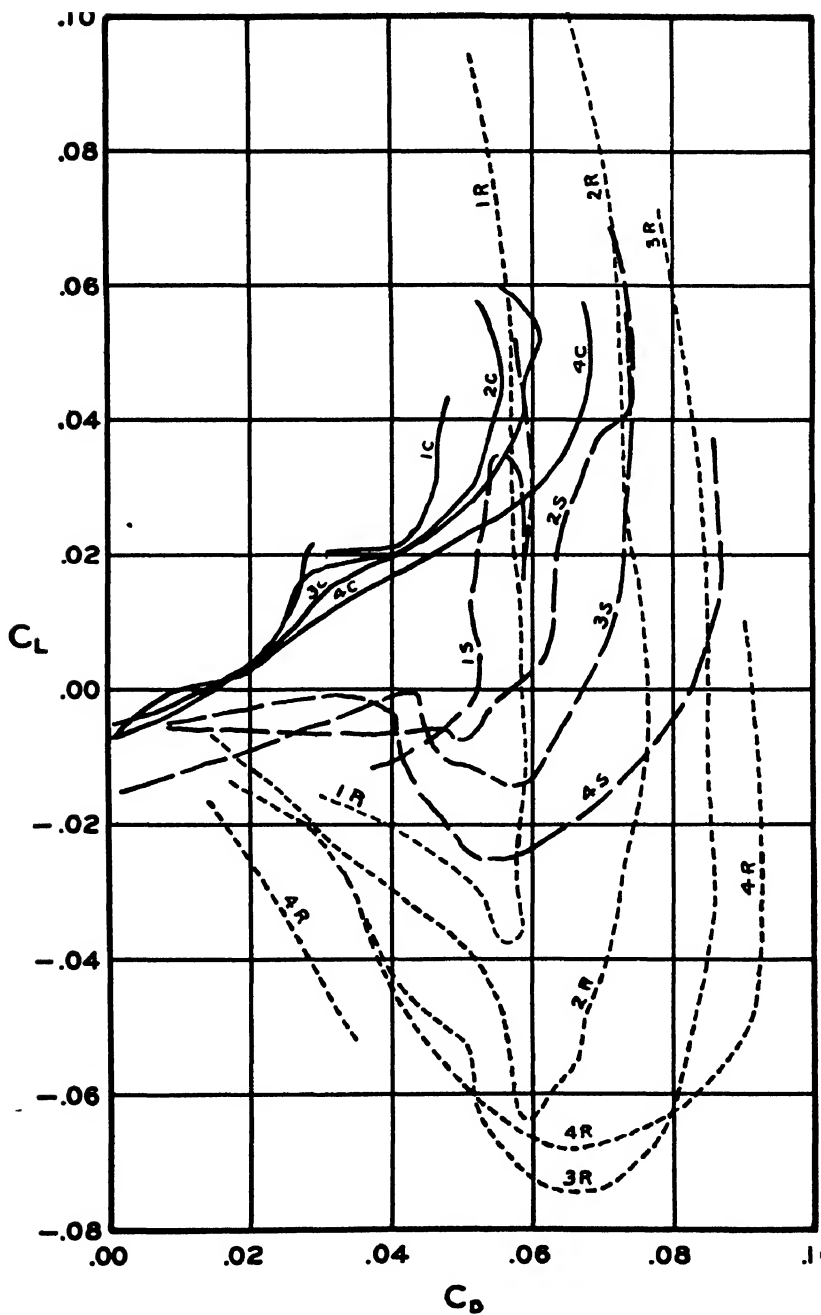
Fig. 13. *Results of force measurements.*

lines of the grid is $\dfrac{5}{36}\,H$ and $\dfrac{10}{36}\,H$ respectively.   In general, the flow past the partial dam is characterized by a change in surface water level, corresponding approximately to the change from maximum potential to maximum kinetic energy.   The nature of the flow is undoubtedly influenced greatly by the downstream conditions, and if the distance to the free fall from the dam were very large, or if an obstruction existed between them, an hydraulic jump would be likely to occur.   Such a jump was easily produced by raising the hinged bottom of the canal model, or by introducing an obstacle downstream from the dam.

Conclusion

It is considered that the force measurements recorded above are sufficiently reliable to be used for engineering design purposes, in the absence of any other data.

The disadvantage of the 2 : 1 rectangular shape from the point of view of the hydrodynamic force is to be noted, and the superior characteristics of the circular shape deserve special attention.

PLATE II
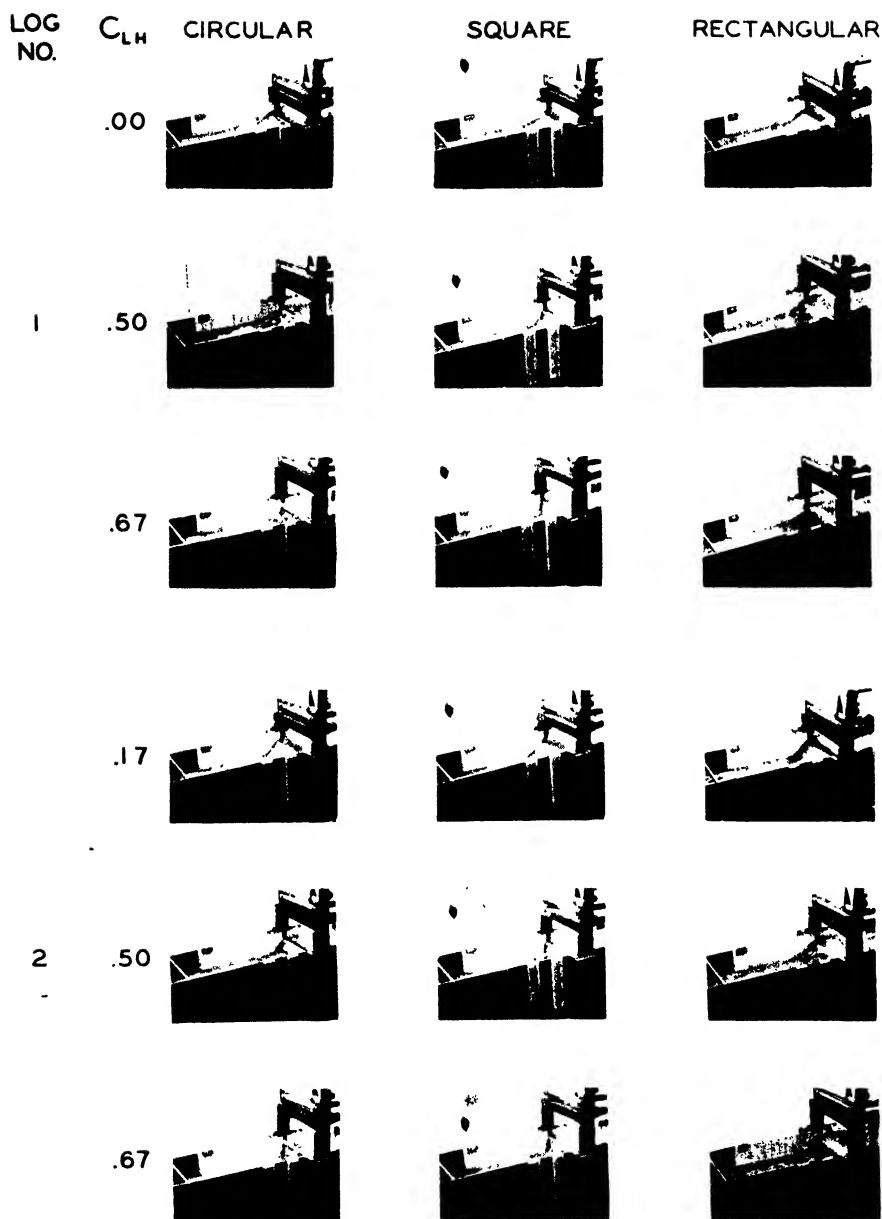
FIG. 14. *Views showing flow of water over log and partial dam.*

PLATE III
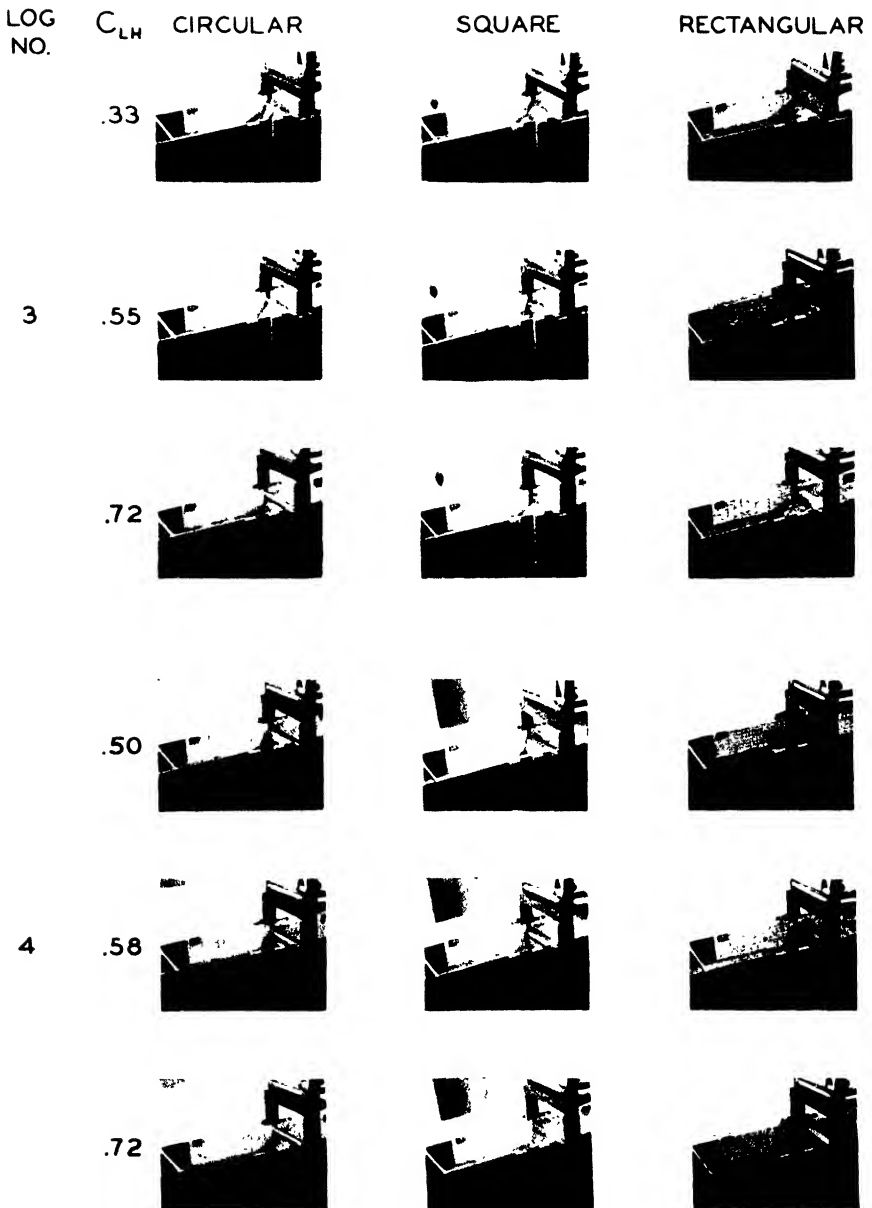
LOG NO.	C_{LH}	CIRCULAR	SQUARE	RECTANGULAR
	.33			
3	.55			
	.72			
	.50			
4	.58			
	.72			

FIG. 15.   *Views showing flow of water over log and partial dam.*

THE SPECTRUM OF DOUBLY IONIZED MERCURY, Hg III[1]

BY MARTIN W. JOHNS[2]

Abstract

The spectrum of mercury, excited in an electrodeless discharge, has been measured from 400 to 11,000 Å. From these data the analysis of Hg III has been extended to include 77 new terms of the configurations $5d^8 6s^2$, $5d^8 6s6p$, $5d^9 7s$, $5d^9 8s$, $5d^9 7p$, $5d^9 6d$, $5d^9 7d$, $5d^9 5f$, and seven unidentified even terms. Isotope shifts have been observed in 11 lines and confirm the classifications of these lines.

Introduction

In 1928 McLennan, McLay, and Crawford (7) classified about 40 of the most prominent ultra-violet lines of Hg III as transitions between the terms of the configurations $5d^9 6s$ and $5d^9 6p$. In 1935 Mack (6) reassigned J-values to two of their $5d^9 6p$ terms; replaced a third; and established the terms $5d^{10} 1_0$ and $5d^9 6p\ 9^0_0$. Recently Ricard (9) published a term scheme for the visible and near ultra-violet lines of Hg III, but did not identify any of the terms.

The present paper confirms the term scheme as established by McLennan, McLay, and Crawford and modified by Mack, with the exception of the term $5d^9 6p\ 9^0_0$, and extends the analysis to include 77 new terms of the configurations $5d^8 6s^2$, $5d^8 6s6p$, $5d^9 7s$, $5d^9 8s$, $5d^9 7p$, $5d^9 6d$, $5d^9 7d$, and $5d^9 5f$ and seven unidentified even terms. This analysis and Ricard's have not as yet been correlated, although the term scheme is confirmed by this investigation.

Experimental

The spectrum emitted by an electrodeless discharge (3) in mercury vapor was measured throughout the spectral region 11,000 to 400 Å. The infra-red and visible regions were photographed using Hilger E_1 quartz and glass prism spectrographs; the near ultra-violet with a 3-metre vacuum grating and an E_1 quartz spectrograph; and the region below 2000 Å with the 3-metre vacuum grating. The fainter lines around 2000 Å were also photographed with small quartz and fluorite spectrographs. Excitation characteristics (3) of the lines were studied in the entire region; these data made it possible to assign the lines fairly definitely to the various spectra, I, II, III, etc., of mercury.

In addition to the above-mentioned measurements, the wave-lengths of ome 300 lines were measured relative to secondary international standards

with a 21 ft. concave grating. These wave-lengths, estimated to be accurate to within 0.003 Å, provided internal standards for use with the prism spectrographs. Some of the lines on the grating plates showed hyperfine structures; when such lines were used as internal standards, these structures were taken into consideration in determining their mean wave-lengths. Internal standards for the vacuum region were obtained from the analysis of Hg II published by McLennan, McLay, and Crawford (8). The terms established by them were evaluated more accurately using the 21 ft. grating measurements. Classified ultra-violet lines, whose frequencies were determined from these term values, provided wave-length standards accurate to within 0.02 Å. In the region below 1000 Å these internal mercury standards were supplemented by Edlén's measurements (4) of the prominent lines of nitrogen, oxygen, and carbon present as impurities in the discharge. Edlén's wave-lengths were found to be in excellent agreement with the mercury standards below 1200 Å. A further check of the consistency of the standards was provided by the agreement of the wave-lengths measured in the first and second orders of the 3-metre vacuum grating.

TABLE I

Configuration	Term Symbol Even	Term Symbol Odd	Term value, cm.⁻¹	Configuration	Term Symbol Even	Term Symbol Odd	Term value, cm.⁻¹
$5d^{10}$	1_0		0.0*			18^o_2	153254.6
$5d^9_{5/2} 6s$	2_3		42850.0*			19^o_3	154214.0
	3_2		46029.7*			20^o_3	155797.0
$5d^9_{3/2} 6s$	4_1		58405.5*			21^o_3	156580.0
	5_2		61085.5*			22^o_2	158205 0
$5d^9_{5/2\,5/2} 6s^2$	6_4		97894.0			23^o_2	160790.5
$5d^9_{5/2} 6p_{1/2}$		1^o_2	103549.1*			24^o_4	161282.2
		2^o_3	105627.5*			25^o_2	161432.0
$5d^9_{5/2\,5/2} 6s^2$	7_2		106028.2			26^o_3	161462.0
$5d^9_{5/2\,3/2} 6s^2$	9_3		112227.1			27^o_4	162155.0
	10_1		117055 1			28^o_2	162972.2
$5d^9_{3/2} 6p_{3/2}$		5^o_4	117994.4*			29^o_4	163452.7
		3^o_2	118547.9*			30^o_2	164905.6
$5d^9_{3/2} 6p_{1/2}$		4^o_1	118607.6*	$5d^8 6s6p$		31^o_3	165004.8
$5d^9_{3/2\,3/2} 6s^2$	11_2		118926.7			32^o_3	166180.0
$5d^9_{5/2} 6p_{3/2}$		6^o_2	120928.1*			33^o_3	166311.1
		7^o_3	121601.9*			34^o_3	167581.0
$5d^9_{3/2\,3/2} 6s^2$	12_4		122340.8			35^o_3	169063.0
$5d^9_{3/2} 6p_{3/2}$		8^o_1	126556.6*			36^o_3	169667.1
$5d^9_{3/2} 6p_{3/2}$		9^o_0	130702.1			37^o_3	171366.6
$5d^9_{3/2\,3/2} 6s^2$	13_2		133731.2			38^o_2	173970.0
$5d^9_{3/2} 6p_{3/2}$		10^o_3	134589.0*			39^o_2	175512.5
		11^o_1	134998.8*			40^o_2	177281.5
		12^o_2	136480.0*			41^o_2	180247.4
		13^o_3	149716.9			42^o_3	183544.0
		14^o_2	150276.0			43^o_3	184698.'
		15^o_2	150279.1			44^o_3	187030
		16^o_1	150857.5			45^o_2	19490
		17^o_1	151997.8			46^o_3	1963·

TABLE I—*(Concluded)*

Configuration	Term Symbol		Term value, cm.⁻¹	Configuration	Term Symbol		Term value, cm.⁻¹
	Even	Odd			Even	Odd	
$5d^9_{5/2}\,7s$	15_3		178428.8			88^o_2	217670.4
	16_2		179038.9	$5d^9_{3/2}\,7p_{3/2}$		89^o_1	217740.2
	17_1		182267.8			90^o_3	218006.5
	18_4		183923.2			91^o_0	218101.5
	19_2		184269.1	$5d^9_{5/2}\,8s$	29_3		221681.4
	20_5		184462.0		30_2		221913.2
$5d^9_{5/2}\,6d$	21_1		184798.6		31_3		224988.1
	22_3		185064.4	$5d^9_{5/2}\,7d$	32^o_2		225489.3
	23_3		186124.2		33_2		225517.1
	24_2		186221.8		34_3		225532.8
	25_4		186520.5	Unknown	35_2		226165.0
	26_0		189775.8		36_3		230369.0
$5d^9_{3/2}\,7s$	27_1		194078.7	$5d^9_{5/2}\,5f$		92^o_1	230416.9
	28_2		194475.9	Unknown	37_3		231588.7
		80^o_1	201800.6			93^o_4	231675.5
		81^o_3	201870.7	$5d^9_{5/2}\,5f$		94^o_3	232102.7
		82^o_2	201883.5			95^o_4	232234.0
$5d^9_{5/2}\,7p$		83^o_2	202090.5		38_4		235017.0
		84^o_4	202357.0	Unknown	39_1		236279.2
		85^o_3	202721.1		40_3		239710.5
$5d^9_{3/2}\,7p_{1/2}$		86^o_2	212421.9		41_1		245631.3
		87^o_1	213660.4	$5d^9\ ^2D_{5/2}$ of Hg IV (approx.) 276000 cm.⁻¹.			

The ordinal numbers 8 and 14 have been reserved for the two unestablished J = 0 terms of $5d^8 6s^2$. The ordinal numbers 47° to 79° have been reserved for unknown terms of $5d^8 6s6p$.
*Established prior to this investigation.

The multiplet terms of Hg III are listed in Table I. The value zero is assigned to the normal state $5d^{10}1_0$; the other term values are relative to this datum. Term values marked with an asterisk were established prior to this investigation. Each term is assigned an ordinal number with its J-value indicated by a subscript. All the terms, except the seven even terms 35_2 to 41_1 inclusive, have been uniquely assigned to the electron configurations which are listed in Column 1. The nomenclature for *jj* coupling has been used in describing all the configurations.

The classified wave-lengths, together with visual estimates of their intensities, their frequencies, and term combinations, are given in Table II. Wave-lengths measured on the 21 ft. grating are given to within 0.001 Å, others to within 0.01 Å. A measure of the accuracy of the measurements is given by the difference "$\nu_{observed} - \nu_{calculated}$" which is tabulated in Column 4.

The unique assignment of the terms to electron configurations is feasible in this spectrum because there is no appreciable overlapping of the terms arising from different configurations of the same parity, and hence no prominent inter-configuration perturbations. If large inter-configuration perturbations were present, terms with the same J-values arising from the perturbing configurations would share their properties, and it then would be meaningless to assign such terms to a single configuration. The distribution

TABLE II

Int.	λ (I.A.)	ν, cm.⁻¹	νobs. −νcalc.	Classification	Int.	λ (I.A.)	ν, cm.⁻¹	νobs. −νcalc.	Classification
1	8451.1	11829.6	− .7	$87_1^0 - 32_2$	4	5372.31	18608.8	.0	$88_2^0 - 39_1$
1	8243.7	12127.1	− 2.2	$7_2^0 - 13_2$ a	5	5272.73	18960.2	− .1	$85_2^0 - 29_3$
20d	8159.5	12252.3	4.1	$12_4 - 10_3^0$ a	30	5210.90	19185.2	.7	$28_2 - 87_1^0$
3d	8084.4	12366.1	3.6	$90_3^0 - 36_3$ a	2	5209.07	19192.0	− .1	$85_2^0 - 30_2$
20	7984.2	12521.3	1.6	$7_2 - 3_2^0$	9	5146.30	19426.0	1.1	$10_1 - 12_2^0$
15	7915.4	12630.1	1.3	$89_1^0 - 36_3$ b	1	5120.77	19522.9	− .5	$13_2 - 18_2^0$
7dd	7808.9	12802.3	− .8	$6_2^0 - 13_2$	2dd	5118.25	19532.5	− .3	$17_1 - 80_1^0$
3	7623.6	13113.5	2.6	$86_2^0 - 34_3$	7	5105.34	19581.9	.2	$27_1 - 87_1^0$
4d	7517.5	13298.6	− .6	$2_3^0 - 11_2$	1	5102.26	19593.7	2.8	$83_2^0 - 29_3$
3d	7401.7	13506.7	.7	$1_2^0 - 10_1$	2	5096.49	19615.9	.2	$17_1 - 82_2^0$
6d	7325.6	13647.0	.0	$10_1 - 9_0^0$	1	5049.53	19798.3	.4	$82_2^0 - 29_3$
20	6709.20	14900.8	.9	$7_2 - 6_2^0$	4	5046.37	19810.7	.0	$81_3^0 - 29_3$
8	6610.05	15124.3	.7	$4_1^0 - 13_2$	5	5043.27	19822.9	{ .1	$17_1 - 83_2^0$
20d	6584.02	15184.1	.8	$3_2^0 - 13_2$				.2	$83_2^0 - 30_2$
30	6512.61	15350.6	.4	$25_4 - 81_3^0$	12	4991.15	20029.9	.2	$82_2^0 - 30_2$
50	6501.26	15377.4	− .2	$1_2^0 - 11_2$ c (5)	8	4987.96	20042.7	.2	$81_3^0 - 30_2$
40	6418.82	15574.9	1.2	$7_2 - 7_3^0$	90	4973.49	20101.0	.5	$6_4 - 5_4^0$ c
3	6388.22	15649.5	− .6	$24_3 - 81_3^0$	12	4869.85	20528.8	.4	$7_2 - 8_1^0$
40	6383.16	15661.9	{ − .4	$11_2 - 10_3^0$	15	4489.67	22267.1	.1	$85_3^0 - 31_3$
			.3	$24_3 - 82_2^0$	30	4470.56	22362.3	.5	$9_3 - 10_3^0$ c
15	6348.78	15746.7	.2	$23_3 - 81_3^0$	2	4420.22	22617.0	− 1.8	$87_1^0 - 39_1$
40	6343.71	15759.3	.0	$23_3 - 82_2^0$	3d	4417.01	22633.4	2.3	$84_4^0 - 31_3$
20	6299.93	15868.8	− .2	$24_3 - 83_2^0$	20	4392.120	22761.67	.0	$16_2 - 80_1^0$
35	6220.24	16072.1	.0	$11_2 - 11_2^0$	2	4390.88	22768.1	− .1	$85_3^0 - 32_2$
30	6170.95	16200.5	− .1	$25_4 - 85_2^0$	15	4385.489	22796.09	.1	$85_2^0 - 33_2$
10	6158.29	16233.8	1.0	$23_3 - 84_4^0$	8d	4382.53	22811.5	− .2	$85_3^0 - 34_3$
2d	6059.12	16499.5	.2	$24_2 - 85_2^0$	25	4378.638	22831.76	.0	$16_2 - 81_3^0$
2d	6041.25	16548.3	.4	$13_2 - 15_1^0$ d	40	4376.186	22844.55	.0	$16_2 - 82_2^0$
10	6023.56	16596.9	.0	$23_3 - 85_3^0$	3d	4375.37	22848.8	.0	$13_2 - 21_2^0$
3	5981 28	16714.2	.7	$2_3^0 - 12_4$	30	4336.881	23051.59	.0	$16_2 - 83_2^0$
5d	5948.33	16806.8	.5	$22_3 - 81_3^0$	6	4326.933	23104.58	.0	$82_2^0 - 31_3$
2	5943.99	16819.1	.0	$22_3 - 82_2^0$	5	4324.57	23117.2	− .2	$81_3^0 - 31_3$
15	5879.83	17002.6	.6	$21_1 - 80_1^0$	5	4313.920	23174.28	− 1.6	$84_4^0 - 34_3$ a
1	5876.16	17013.2	2.7	$90_3^0 - 38_4$	1	4310.16	23194.5	− 1.0	$28_2 - 88_2^0$
10d	5851.61	17084.6	− .3	$21_1 - 82_2^0$	5	4297.25	23264.2	− .1	$28_2 - 89_1^0$
2	5837.80	17125.0	− 1.3	$13_2 - 16_1^0$	3	4267.28	23427.6	.8	$83_2^0 - 33_2$ e
6	5781.12	17292.9	{ .3	$22_3 - 84_4^0$	35	4264.674	23441.88	.0	$15_3 - 81_3^0$
			1.0	$21_1 - 83_2^0$	1	4264.27	23444.1	.2	$85_3^0 - 35_2$
2	5695.68	17552.3	− 1.0	$11_2 - 12_2^0$	8	4262.346	23454.68	.0	$15_3 - 82_2^0$
10	5679.47	17602.4	.6	$19_2 - 81_3^0$	1	4248.58	23530.7	1.3	$28_2 - 90_3^0$
15	5661.99	17656.7	.0	$22_3 - 85_2^0$	15	4237.424	23592.62	.9	$27_1 - 88_3^0$
10	5571.06	17944.9	{ − 1.1	$28_2 - 86_2^0$	3	4234.79	23607.3	1.5	$82_2^0 - 32_2$
			1.2	$10_1 - 11_1^0$	5	4232.735	23618.76	.1	$81_3^0 - 32_2$
5d	5570.11	17948.0	{ .5	$18_4 - 81_3^0$	25	4230.086	23633.55	.0	$82_2^0 - 33_2$
			.9	$86_2^0 - 36_3$	10	4227.800	23646.33	− .1	$81_3^0 - 33_2$
1	5500.36	18175.6	2.1	$91_0^0 - 39_1$	20	4227.243	23649.44	.1	$82_2^0 - 34_3$
5	5473.18	18265.9	− .7	$13_2 - 17_1^0$				.1	$81_3^0 - 34_3$
30	5450.210	18342.83	− .4	$27_1 - 86_2^0$	3	4224.96	23662.2	{ .5	$15_3 - 83_2^0$
5	5418.09	18451.6	− .4	$19_2 - 85_3^0$				.7	$27_1 - 89_1^0$
1	5392.77	18538.2	− .8	$89_1^0 - 39_1$	15	4221.412	23682.11	− .1	$16_2 - 85_3^0$

TABLE II—(Continued)

Int.	λ (I.A.)	ν, cm.⁻¹	νobs. − νcalc.	Classification	Int	λ (I.A.)	ν, cm.⁻¹	νobs. − νcalc.	Classification
80	4216.74	23708.4	.5	$6_4 - 7^{\circ}_3$ c	2	3016.06	33146.2	− .1	$81^{\circ}_3 - 38_4$
1	4198.63	23810.6	2.6	$84^{\circ}_4 - 35_2$	1	3001.84	33303.2	.6	$21_1 - 91^{\circ}_0$
6	4185.493	23885.34	.7	$26_0 - 87^{\circ}_1$	3	2994.49	33385.0	2.0	$16_2 - 86^{\circ}_2$ d
30	4177.994	23928.21	.0	$15_3 - 84^{\circ}_4$	2	2993.01	33401.5	.2	$19_2 - 88^{\circ}_2$
7	4161.586	24022.55	.0	$27_1 - 91^{\circ}_0$	1	2988.06	33456.8	.6	$12_4 - 20^{\circ}_2$
1	4152.42	24075.6	1.1	$83^{\circ}_3 - 35_2$	1	2986.57	33473.5	2.4	$19_2 - 89^{\circ}_1$
40	4122.10	24252.7	− .2	$9_3 - 12^{\circ}_3$ c	1	2963.21	33737.4	.0	$19_2 - 90^{\circ}_3$
3	4117.24	24281.3	− .2	$82^{\circ}_2 - 35_2$	6	2957.36	33804.1	1.7	$10_1 - 16^{\circ}_1$
25	4115.373	24292.30	.0	$15_3 - 85^{\circ}_3$	2	2933.17	34082.9	− .4	$18_4 - 90^{\circ}_3$
1	4115.07	24294.1	− .2	$81^{\circ}_3 - 35_2$	1	2912.21	34328.2	.3	$11_2 - 18^{\circ}_2$
15	3651.731	27376.50	.4	$12_4 - 13^{\circ}_3$	1	2829 51	35331.4	.4	$13_2 - 35^{\circ}_2$ d
1	3643.44	27438.8	.2	$24_2 - 87^{\circ}_1$	1	2823.71	35404.0	1.0	$17_1 - 88^{\circ}_2$
1	3619.03	27623.9	.6	$21_1 - 86^{\circ}_2$	1	2818.07	35474.9	2.5	$17_1 - 89^{\circ}_1$
7	3615.849	27648.17	.3	$85^{\circ}_3 - 36_3$	6	2781.92	35935.8	− .1	$13_2 - 36^{\circ}_3$
6	3609.07	27700.1	− .7	$13_2 - 25^{\circ}_2$	20	2724.39	36694.6	− .4	$6_4 - 10^{\circ}_2$ c
20	3578.738	27934.86	− .4	$12_4 - 14^{\circ}_4$	1d	2702.71	36989.0	− .4	$85^{\circ}_3 - 40_3$
1	3568.85	28012.3	.3	$84^{\circ}_4 - 36_3$	1	2676.28	37354.2	.6	$84^{\circ}_4 - 40_3$
6	3557.24	28103.7	.0	$2_3 - 13_2$ c	1	2666.78	37487.3	− 2 5	$9_3 - 13^{\circ}_2$
1	3551.09	28152.4	− .4	$19_2 - 86^{\circ}_2$	1	2657.41	37619.4	.3	$83^{\circ}_2 - 40_3$
2	3535.39	28277.4	− 1.1	$83^{\circ}_2 - 36_3$	1	2656.29	37635.3	− .1	$13_2 - 37^{\circ}_3$
1	3509.29	28487.7	2.2	$82^{\circ}_2 - 36_3$	2d	2642.72	37828.5	1.5	$82^{\circ}_2 - 40_3$
5	3507.97	28498.4	.1	$81^{\circ}_3 - 36_3$	1	2641.93	37839.9	.1	$81^{\circ}_3 - 40_3$
4d	3500.34	28560.5	− .3	$7_2 - 10^{\circ}_3$ c	2	2627.36	38049.7	.8	$9_3 - 14^{\circ}_4$
1	3499.33	28568.8	.4	$80^{\circ}_1 - 36_3$ f	2	2587.76	38631.9	.4	$16_2 - 88^{\circ}_2$
2	3464.00	28860.1	− 1.7	$21_1 - 87^{\circ}_1$	3	2567.19	38941.4	.0	$12_4 - 24^{\circ}_2$
30	3462.936	28869.0	1.4	$85^{\circ}_3 - 37_3$ a	1	2566.08	38958.3	.7	$16_2 - 90^{\circ}_3$
8d	3450.76	28970.8	.2	$7_2 - 11^{\circ}_1$ c	1	2547.45	39243.2	1.6	$15_3 - 88^{\circ}_2$
30	3419.983	29231.56	− .2	$84^{\circ}_4 - 37_3$	5	2545.16	39278.5	.2	$11_2 - 22^{\circ}_2$
10	3418.69	29242.57	1.6	$13_2 - 28^{\circ}_2$ d	1	2510.90	39814.4	.2	$12_4 - 27^{\circ}_4$
15	3401.314	29392.00	.7	$19_2 - 87^{\circ}_1$	2	2459.80	40641.4	.3	$26_0 - 92^{\circ}_1$
4	3388.984	29498.93	1.0	$83^{\circ}_2 - 37_3$	3	2436.02	41038.1	.6	$9_3 - 18^{\circ}_2$ d
2	3365.45	29705.2	.0	$82^{\circ}_2 - 37_3$	8	2431.65	41111.9	.0	$6_4 - 29^{\circ}_4$
1	3315.32	30154.4	.3	$17_1 - 86^{\circ}_2$	4	2392.72	41780 7	− .6	$13_2 - 39^{\circ}_2$
10d	3312.27	30182.1	.0	$1^{\circ}_2 - 13_2$ c	1	2388.11	41861.3	− 2.5	$11_2 - 23^{\circ}_2$
2	3283.01	30451.1	− .7	$7_2 - 12^{\circ}_2$	5	2383.10	41949.3	.5	$12^{\circ}_2 - 15_3$
10	3246.95	30789.3	.3	$11_2 - 13^{\circ}_3$	6d	2380.98	41986.7	− .2	$9_3 - 19^{\circ}_3$ d
1	3206.85	31174.3	− .1	$13_2 - 30^{\circ}_2$	75	2354.238	42463.58	.0	$5_2 - 1^{\circ}_2$
3	3197.67	31273.6	.0	$13_2 - 31^{\circ}_3$	2	2351.90	42505.8	.5	$11_2 - 25^{\circ}_2$
1	3188.53	31353.4	1.0	$11_2 - 15^{\circ}_1$	1	2350.26	42535.4	.1	$11_2 - 26^{\circ}_2$ d
2	3175.17	31485.3	− .7	$25_4 - 90^{\circ}_3$ d	1	2343.21	42663.4	− .6	$12_4 - 31^{\circ}_2$
1	3172.02	31516.6	− 1.8	$24_2 - 89^{\circ}_1$ d	1	2295.98	43540.9	.1	$83^{\circ}_2 - 41_1$
1	3136.44	31874.1	.9	$12_4 - 19^{\circ}_3$	1	2295.57	43548.7	− .6	$13_2 - 40^{\circ}_2$
1	3130.87	31930.8	.0	$11_2 - 16^{\circ}_1$	20	2294.45	43570.0	.1	$9_3 - 20^{\circ}_3$
1	3126.90	31971.3	.4	$87^{\circ}_1 - 41_1$	2d	2285.64	43737.9	2.5	$10_1 - 23^{\circ}_2$
4	3095.46	32296.0	.1	$85^{\circ}_3 - 38_4$	1	2285.12	43747.8	.0	$82^{\circ}_2 - 41_1$
4	3080.71	32450.6	1.8	$13_2 - 32^{\circ}_3$	1	2280.77	43831.3	.6	$80^{\circ}_1 - 41_1$
1	3060.96	32660.0	.0	$84^{\circ}_4 - 38_4$	3	2280.33	43839.7	− .1 .5	$10^{\circ}_3 - 15_3$ $12_4 - 32^{\circ}_2$
6	3034.73	32942.3	.2 .7	$22_3 - 90^{\circ}_3$ $21_1 - 89^{\circ}_1$	15	2269.92	44040.8	.7	$11^{\circ}_1 - 16_2$
3	3022.86	33071.7	.6	$11_2 - 17^{\circ}_1$	1	2269.68	44045.4	− .1	$11_2 - 28^{\circ}_2$

TABLE II—(Continued)

Int.	λ(I.A.)	ν, cm.⁻¹	νobs.−νcalc.	Classification	Int.	λ(vac.)	ν, cm.⁻¹	νobs.−νcalc.	Classification
1	2249.00	44450.4	− .5	$10_3^0 - 16_2$	15	1826.08	54762.1	− .2	$7_2 - 23_2^0$
75	2244.375	44541.98	.0	$5_2 - 2_3^0$	2	1825.59	54776.8	.2	$11_1^0 - 26_0$
20	2214.46	45143.6	.0	$4_1 - 1_3^0$	1	1806.55	55354.1	.2	$9_3 - 34_3^0$
5	2194.64	45551.3	.0	$23_3 - 93_4^0$	15	1803.95	55433.9	.1	$7_2 - 26_3^0$
1	2191.43	45618.0	− .3	$21_1 - 92_1^0$	2	1775.57	56319.9	− .1	$6_4 - 19_3^0$
3	2186.89	45712.9	− .6	$25_4 - 95_4^0$	1	1767.22	56586.1	.3	$11_2 - 39_2^0$
3	2183.31	45787.6	− .2	$12_2^0 - 17_1$	15	1759.75	56826.3	− .6	$7_3 - 15_3$
1	2178.86	45881.1	.2	$24_2 - 94_2^0$	1	1759.44	56836.3	.4	$9_3 - 35_2^0$
			− .1	$11_2 - 30_2^0$	10	1756.09	56944.7	.7	$7_2 - 28_2^0$
2	2174.24	45978.8	.3	$23_3 - 94_2^0$				.6	$7_3^0 - 16_2$
			.9	$8_3 - 22_2^0$	12d	1741.02	57437.6	− 2.4	$9_3 - 36_3^0$
8	2169.51	46078.8	.7	$11_2 - 31_3^0$	40	1740.27	57462.3	− .1	$5_2 - 3_2^0$
1	2168.08	46109.2	− .6	$23_3 - 95_4^0$	2	1739.11	57500.7	.0	$6_2^0 - 15_3$
12	2166.27	46147.8	− .0	$19_2 - 92_1^0$				1.5	$3_2 - 1_2^0$
3	2149.15	46515.3	− .9	$13_2 - 41_1^0$	75	1738.50	57520.9	− 1.2	$5_2 - 4_1^0$
1	2144.69	46612.0	.1	$22_3 - 93_4^0$	4	1736.16	57598.4	− .3	$12_2^0 - 27_1$
1d	2125.21	47039.3	.9	$22_3 - 94_2^0$	15	1727.04	57902.5	− .5	$6_4 - 20_3^0$
4d	2119.32	47170.0	.4	$22_3 - 95_4^0$	5	1724.21	57997.6	1.7	$12_2^0 - 28_2$
10	2116.34	47236.4	.0	$7_2 - 18_2^0$	8	1720.86	58110.5	− .3	$6_2^0 - 16_2$
1	2115.59	47253.1	− .2	$11_2 - 31_3^0$	8	1716.99	58241.5	.5	$8_1^0 - 21_1$
5	2113.31	47304.1	.0	$21_1 - 94_2^0$	2	1713.68	58354.0	− .8	$11_2 - 40_2^0$
1	2112.33	47326.0	− .3	$12_4 - 33_3^0$	2	1703.98	58686.1	.1	$6_4 - 21_3^0$
1	2093.46	47752.6	.3	$18_4 - 93_4^0$	15	1692.60	59080.7	.8	$11_1^0 - 27_1$
2	2092.59	47772.4	.4	$20_5 - 95_4^0$	1	1688.02	59241.0	1.5	$9_3 - 37_2^0$
1	2089.99	47831.8	− 1.8	$19_2 - 94_2^0$	9	1681.40	59474.2	− 2.9	$11_1^0 - 28_2$
4d	2074.60	48186.6	.8	$7_2 - 19_3^0$	50	1677.90	59598.3	.5	$3_2 - 2_3^0$
1	2069.19	48312.6	1.8	$18_4 - 95_4^0$	10dd	1676.01	59665.5	.3	$8_1^0 - 24_2$
8	2058.48	48563.9	.5	$9_3 - 23_2^0$	40	1671.06	59842.3	− .3	$5_2 - 6_2^0$
10	2054.66	48654.2	− .1	$11_2 - 34_3^0$	15d	1669.82	59836.7	− .2	$10_3^0 - 28_2$
1	2037.81	49056.5	1.4	$9_3 - 24_4^0$	40	1662.72	60142.4	.0	$4_1 - 3_2^0$
2	2031.65	49205.2	.3	$9_3 - 25_2^0$	1	1658.85	60282.7	− .2	$7_2 - 33_2^0$
2	2030.44	49234.5	− .5	$9_3 - 26_2^0$				1.9	$4_1^0 - 16_2 \, d$
3	2029.55	49256.0	− 1.0	$10_1 - 33_2^0 \, d$	20	1654.72	60433.2	− 1.2	$5_4^0 - 15_3$
1	2013.69	49644.0	.2	$12_2^0 - 23_3$	8	1653.14	60490.9	− .1	$3_2^0 - 16_2$
7	2008.63	49769.0	.2	$7_2 - 20_3^0$	20	1652.45	60516.3	− .2	$5_2 - 7_3^0$
5	2007.42	49799.0	− .8	$11_1^0 - 21_1$	60	1647.47	60699.1	.0	$2_3 - 1_2^0$
3	2006.91	49812.7	.1	$13_2 - 42_3^0$	3	1634.68	61174.1	.6	$13_2 - 45_2^0$
3	2004.61	49868.8	.9	$9_3 - 27_4^0 \, d$	3	1630.30	61338.4	− 1.3	$6_2^0 - 17_1$
	λ(vac.)				1	1624.63	61552.5	− .3	$7_2 - 34_3^0$
1	1981.17	50475.2	− .3	$10_3^0 - 22_3$	1	1619.64	61742.1	− .8	$9_3 - 38_2^0$
2	1970.64	50744.9	− .2	$9_3 - 28_2^0$	7	1604.62	62320.1	− 1.2	$7_3^0 - 18_4$
3	1952.16	51225.3	2.3	$11_1^0 - 24_2$	50	1599.44	62521.9	− .7	$4_1 - 6_2^0$
1	1925.43	51942.0	.5	$10_3^0 - 25_4$	3	1596.21	62648.4	1.1	$13_2 - 46_2^0$
4	1916.56	52176.8	.0	$7_2 - 22_2^0$	8	1595.73	62667.2	.0	$7_3^0 - 19_2 \, d$
1	1906.93	52440.3	.4	$11_2 - 37_2^0$	30	1592.93	62777.4	− .1	$2_3 - 2_3^0$
4	1905.41	52482.1	− .2	$8_1^0 - 16_2$	1	1586.36	63037.4	2.6	$7_2 - 35_3^0 \, g$
3	1898.30	52678.7	.2	$9_3 - 30_2^0$	5	1582.46	63192.8	.5	$10_1 - 41_2^0$
6	1894.77	52776.9	− .8	$9_3 - 31_2^0$	2	1581.76	63220.7	1.5	$8_1^0 - 26_0 \, d$
3	1853.46	53953.1	.2	$9_3 - 32_2^0$	3	1580.10	63287.1	1.7	$9_3 - 39_2^0$
10	1848.95	54084.8	.8	$9_3 - 33_2^0$	3b	1577.95	63373.4	− 3.2	$9_0^0 - 27_1$

TABLE II—(Continued)

Int.	λ(vac.)	ν, cm.⁻¹	νobs. − νcalc.	Classification	Int.	λ(vac.)	ν, cm.⁻¹	νobs. − νcalc.	Classification
1	1577.58	63388.2	.0	$6_4 - 24^0_4$ d	40	1335.08	74901.9	3.5	$3_2 - 6^0_2$
9	1575.73	63462.6	.1	$7^0_3 - 22_3$	40	1330.77	75144.5	.1	$2_3 - 5^0_4$
8	1573.12	63567.9	− .1	$6_4 - 26^0_3$	25	1326.36	75394.3	− .2	$5_2 - 12^0_2$
1	1571.36	63639.1	.2	$7_2 - 36^0_3$	2	1324.68	75490.0	.2	$1^0_2 - 16_2$
3	1570.87	63659.0	− 1.2	$4^0_1 - 17_1$	4d	1323.97	75530.4	− .4	$3^0_2 - 27_1$ e
5	1569.39	63719.0	− .9	$3^0_2 - 17_1$	30	1323.22	75573.3	1.1	$3_2 - 7^0_2$
4	1565.67	63870.4	− .1	$6^0_2 - 21_1$	30	1321.04	75697.9	.0	$2_3 - 3^0_2$
5	1556.17	64260.3	− .7	$6_4 - 27^0_2$	3	1318.07	75868.5	.2	$4^0_1 - 28_2$
15	1549.85	64522.4	.1	$7^0_3 - 23_3$	2	1317.03	75928.4	.4	$3^0_2 - 28_2$
3	1547.51	64619.9	{ .0	$7^0_3 - 24_2$	30	1305.60	76593.2	− .1	$4_1 - 11^0_1$
			2.6	$10_2 - 42^0_3$	5	1290.07	77515.2	− .6	$7_2 - 42^0_3$
20	1540.37	64919.5	.7	$7^0_3 - 25_4$	1	1284.57	77847.1	3.5	$10_1 - 45^0_2$ g
2	1537.14	65055.9	1.5	$9_3 - 40^0_2$	30d	1280.80	78076.2	{ − 1.9	$2_3 - 6^0_2$
15	1533.84	65195.8	− .3	$6^0_2 - 23_3$				1.7	$4_1 - 12^0_2$
12	1531.53	65294.2	.5	$6^0_2 - 24_2$	20	1277.19	78296.9	1.2	$2^0_3 - 18_4$
25	1530.49	65338.6	.2	$7_2 - 37^0_3$	7	1271.58	78642.3	.7	$2^0_3 - 19_2$
40	1527.40	65470.5	− .6	$5_2 - 8^0_1$	4	1271.12	78670.8	.3	$7_2 - 43^0_3$
12	1525.35	65558.8	.1	$6_4 - 29^0_4$	8	1270.33	78719.7	1.0	$1^0_2 - 17_1$
2	1521.59	65720.7	− .5	$3^0_2 - 19_2$	25	1269.78	78753.5	1.6	$2_3 - 7^0_3$
3	1520.41	65771.7	− .3	$11_2 - 43^0_3$	10	1258.86	79437.0	.1	$2^0_3 - 22_3$
8	1516.80	65928.2	− .6	$5^0_4 - 18_4$	2	1242.30	80495.9	− .8	$2^0_3 - 23_3$
7	1510.79	66190.6	− .4	$4^0_1 - 21_1$	15	1241.81	80527.6	.7	$3_2 - 8^0_1$
5	1509.45	66249.3	− 1.4	$3^0_2 - 21_1$	7	1238.84	80720.7	.7	$1^0_2 - 19_2$
10	1504.48	66468.0	.4	$5^0_2 - 20_5$	2	1236.18	80894.4	1.4	$2^0_3 - 25_4$
4	1503.38	66516.8	.3	$3^0_2 - 22_3$	2	1234.53	81002.5	.7	$7_2 - 44^0_3$ g
6	1490.95	67071.4	1.4	$5^0_4 - 22_3$	9d	1230.77	81249.9	.4	$1^0_2 - 21_1$
15	1479.81	67576.3	.0	$3^0_2 - 23_3$	12	1226.75	81516.2	.9	$1^0_2 - 22_3$
10	1478.97	67614.6	.4	$4^0_1 - 24_2$	3	1209.52	82677.4	− .2	$9_3 - 45^0_2$
20	1477.75	67670.4	3.5	$3^0_2 - 24_2$ d	1	1188.35	84150.4	− 1.0	$9_3 - 46^0_2$ g
3	1470.13	68021.2	.9	$9_3 - 41^0_2$	2	1180.00	84745.8	− .7	$10_1 - 80^0_1$
1	1467.78	68130.1	.3	$5^0_2 - 23_3$	8	1167.53	85650.9	− .1	$6_4 - 42^0_3$
25	1467.33	68151.0	− .1	$4_1 - 8^0_1$	8	1152.01	86804.8	.1	$6_4 - 43^0_3$
15	1459.30	68526.0	− .1	$5^0_2 - 25_4$	1	1129.16	88561.4	2.1	$3_2 - 10^0_3$
12d	1434.98	69687.4	.4	$6_4 - 34^0_3$	3	1125.16	88876.2	− .3	$7_2 - 45^0_2$
10	1405.11	71168.8	{ − .2	$6_4 - 35^0_3$	2	1123.99	88968.8	− .3	$3_2 - 11^0_1$
			.6	$4^0_1 - 26_0$	5	1121.90	89134.5	− 1.5	$6_4 - 44^0_3$
2	1403.42	71254.5	1.2	$7_2 - 40^0_2$	1	1115.52	89644.3	.5	$9_3 - 81^0_2$
8	1393.28	71773.1	.0	$6_4 - 36^0_3$	5	1109.48	90132.3	− .6	$9_3 - 84^0_2$
25	1383.19	72296.6	.0	$4_1 - 9^0_0$	1	1106.81	90349.8	− .5	$7_2 - 46^0_2$
40	1378.96	72518.4	.2	$3_2 - 3^0_2$	8	1105.58	90450.3	.0	$3_2 - 12^0_2$
40	1377.83	72577.9	.2	$3_2 - 4^0_1$	7	1105.03	90495.3	1.3	$9_3 - 85^0_2$
10	1373.60	72801.4	.1	$2^0_3 - 15_3$	5	1090.07	91737.3	− 1.7	$2_3 - 10^0_3$
20	1367.02	73151.8	1.2	$6^0_2 - 27_1$	1	1081.63	92453.0	.5	$4_1 - 16^0_2$
10	1362.19	73411.2	− .2	$2^0_3 - 16_2$	2	1068.47	93591.7	− .6	$4_1 - 17^0_2$
40	1360.46	73504.5	1.0	$5_2 - 10^0_3$	5	1068.05	93630.3	.3	$2_3 - 12^0_2$
3	1359.65	73548.3	.5	$6^0_2 - 28_2$	4	1047.19	95493.7	− .8	$5_2 - 21^0_2$
1	1359.20	73572.6	.0	$6_4 - 37^0_3$	1	1044.54	95735.9	3.5	$7_2 - 80^0_1$
20	1352.93	73913.6	.3	$5_2 - 11^0_2$	3	1043.23	95856.1	.8	$7_2 - 82^0_2$
4	1347.35	74219.7	.5	$7_2 - 41^0_2$	6	1040.96	96065.1	2.8	$7_2 - 83^0_2$
5	1336.84	74803.3	.4	$9_3 - 44^0_3$	2	1034.16	96696.9	4.0	$7_2 - 85^0_2$
20	1335.50	74878.4	− 1.3	$1^0_2 - 15_3$ e	5	1029.66	97119.4	− .1	$5_2 - 22^0_2$

TABLE II—(Concluded)

Int.	λ(vac.)	ν, cm.$^{-1}$	$\nu_{obs.} - \nu_{calc.}$	Classification
3	999.26	100074	— .5	$7^{\circ}_{3} - 29_{3}$
8	996 94	100307	— 4	$7^{\circ}_{3} - 30_{2}$
10	996.51	100350	3	$5_{2} - 25^{\circ}_{2}$
3	996.25	100376	0	$5_{2} - 26^{\circ}_{2}$
8	969.63	103132	— 1	$3^{\circ}_{2} - 29_{3}$
1	967.99	103307	1	$4^{\circ}_{1} - 30_{3}$
8	967.43	103367	2	$3^{\circ}_{2} - 30_{2}$
4	964 44	103687	0	$5^{\circ}_{4} - 29_{3}$
			0	$3_{2} - 13^{\circ}_{3}$
1	961.88	103965	−11	$6_{4} - 81^{\circ}_{3}$ h
2	959.26	104247	— 2	$3_{2} - 15^{\circ}_{1}$
10	957.36	104454	— 9	$6_{4} - 84^{\circ}_{4}$
1	956.33	104566	3	$7^{\circ}_{3} - 35_{2}$
			0	$4_{1} - 28^{\circ}_{2}$
2	953.95	104827	0	$6_{4} - 85^{\circ}_{3}$
			0	$3_{2} - 16^{\circ}_{1}$
1	943.70	105966	— 2	$3_{2} - 17^{\circ}_{1}$
1	939.94	106390	— 3	$7_{2} - 86^{\circ}_{2}$
3	935.74	106867	0	$2_{3} - 13^{\circ}_{3}$
4	935.10	106940	— 1	$3^{\circ}_{2} - 32_{3}$
2	930.90	107423	— 3	$2_{3} - 14^{\circ}_{4}$
1	926.08	107982	4	$5_{2} - 35^{\circ}_{3}$
6	911.03	109766	— 1	$3_{2} - 20^{\circ}_{3}$
3d	904.55	110552	2	$3_{2} - 21^{\circ}_{3}$
4	903.70	110656	— 4	$6^{\circ}_{2} - 37_{3}$
6	891.47	112174	— 1	$3_{2} - 22^{\circ}_{2}$
2	889.82	112382	7	$5^{\circ}_{4} - 36_{3}$
2	885.86	112885	0	$5_{2} - 38^{\circ}_{2}$
10	885.38	112946	— 1	$2_{3} - 20^{\circ}_{0}$
2	881.72	113415	0	$7^{\circ}_{3} - 38_{4}$
1	879.29	113728	— 2	$2_{3} - 21^{\circ}_{3}$
2	873.90	114430	3	$5_{2} - 39^{\circ}_{3}$
4	866.91	115352	— 3	$2_{3} - 22^{\circ}_{3}$
			1	$6^{\circ}_{2} - 39_{1}$
8	866.31	115432	0	$3_{2} - 26^{\circ}_{3}$
3	861.67	116054	0	$2^{\circ}_{3} - 29_{3}$
4d	859.96	116284	— 2	$2^{\circ}_{3} - 30_{2}$
15	855.11	116944	1	$3_{2} - 28^{\circ}_{2}$
4	846.52	118131	— 1	$1^{\circ}_{2} - 29_{3}$
1	844.89	118359	— 5	$1^{\circ}_{2} - 30_{2}$
30	843.11	118608	— 3	$2_{3} - 26^{\circ}_{3}$
			0	$1_{0} - 4^{\circ}_{1}$
4	841.21	118876	0	$4_{1} - 40^{\circ}_{2}$
			0	$3_{2} - 30^{\circ}_{2}$
8	839.20	119161	— 1	$5_{2} - 41^{\circ}_{3}$
1	838.21	119302	— 3	$2_{3} - 27^{\circ}_{4}$
2	837.81	119359	— 2	$2^{\circ}_{3} - 31_{3}$
2	832 47	120124	2	$2_{3} - 28^{\circ}_{2}$

Int.	λ(vac.)	ν, cm.$^{-1}$	$\nu_{obs.} - \nu_{calc.}$	Classification
3	823.44	121442	3	$1^{\circ}_{2} - 31_{3}$
15	822.69	121552	1	$3_{2} - 34^{\circ}_{3}$
2	820.37	121843	1	$4_{1} - 41^{\circ}_{2}$
1	815.53	122620	4	$1^{\circ}_{2} - 35_{3}$ h
20	812.84	123025	— 8	$3_{2} - 35^{\circ}_{3}$ g
5	810.85	123327	— 3	$2_{3} - 32^{\circ}_{2}$
1	809.85	123480	9	$2_{3} - 33^{\circ}_{3}$
15	808.82	123637	0	$3_{2} - 36^{\circ}_{3}$
2	801.72	124732	1	$2_{3} - 34^{\circ}_{3}$
1	793.91	125959	— 2	$2^{\circ}_{3} - 37_{3}$
1	792.31	126213	0	$2_{3} - 35^{\circ}_{3}$
6	790.17	126555	— 2	$1_{0} - 8^{\circ}_{1}$
6	788.53	126818	— 2	$1^{\circ}_{2} - 36_{3}$
			1	$2_{3} - 36^{\circ}_{3}$
1	781.00	128041	1	$1^{\circ}_{2} - 37_{3}$
2	772.82	129396	6	$2^{\circ}_{3} - 38_{4}$
2	772.32	129480	— 3	$3_{2} - 39^{\circ}_{3}$
3	762.68	131117	— 3	$2_{3} - 38^{\circ}_{2}$
1	761.89	131253	1	$3_{2} - 40^{\circ}_{3}$
1	760.65	131467	— 1	$1^{\circ}_{2} - 38_{4}$ f
3	753.79	132663	0	$2_{3} - 39^{\circ}_{2}$
2	745.83	134079	— 4	$2^{\circ}_{3} - 40_{3}$
5	745.06	134217	0	$3_{2} - 41^{\circ}_{2}$
8	740.75	134998	— 1	$1_{0} - 11^{\circ}_{1}$
2	734.43	136160	— 1	$1^{\circ}_{2} - 40_{3}$
4	727.86	137389	2	$2_{3} - 41^{\circ}_{2}$
3	721.17	138664	— 5	$3_{2} - 43^{\circ}_{3}$
6	714 27	140003	— 3	$2^{\circ}_{3} - 41_{1}$ f
2	710.30	140786	1	$5_{2} - 81^{\circ}_{3}$
6	706.13	141617	−19	$5_{2} - 85^{\circ}_{3}$ a
5	705.00	141844	— 5	$2_{3} - 38^{\circ}_{3}$
2	703.85	142076	— 6	$1^{\circ}_{2} - 41_{2}$
3	696.96	143480	2	$4_{1} - 82^{\circ}_{1}$
1	695.93	143693	8	$4_{1} - 83^{\circ}_{3}$
4	693.61	144173	— 7	$2_{3} - 44^{\circ}_{3}$
2	660.79	151334	— 2	$5_{2} - 86^{\circ}_{2}$
2	649.35	154000	−16	$4_{1} - 86^{\circ}_{3}$ h
2	641.97	155769	— 2	$3_{2} - 80^{\circ}_{1}$
4	641.62	155856	15	$3_{2} - 81^{\circ}_{3}$
			2	$3_{2} - 82^{\circ}_{3}$
3	640.76	156065	4	$3_{2} - 83^{\circ}_{3}$ h
3	628.89	159010	−10	$2_{3} - 81^{\circ}_{3}$
2	626.93	159507	0	$2_{3} - 84^{\circ}_{4}$ h
10	626.17	159700	4	$4_{1} - 91^{\circ}_{0}$
2	589.78	169555	−17	$2_{3} - 86^{\circ}_{3}$ h
2	572.09	174798	−22	$2_{3} - 88^{\circ}_{3}$ h
1	570.91	175159	2	$2_{3} - 90^{\circ}_{3}$ h

a Doubtful.
b Too intense for this transition.
c Wide hyperfine structure.
d Also classified in Hg II.
e Coincides with C II line.
f Forbidden by J selection rule.
g Also classified in Hg IV.
h Bloch's measurement (1).

and combining properties of the terms are consistent with the distributions in the iso-electronic spectra, chiefly Au II, Bi V, and Pb VI, and in the I and II spectra of mercury. The multiplet separation of all the identified configurations with the exception of $5d^86s6p$ indicate that the coupling tends towards jj. In view of this, the nomenclature for jj coupling has been used, though its use is not to be interpreted as signifying strict jj coupling.

Mack's choice of the $J=0$ term of $5d^96p$, in his nomenclature 9_0^0 with the value 129080.9, has been discarded and replaced by a new one. His choice was based on the one line λ 1414.92 as the transition $5d^96s\,4_1 - 5d^96p\,9_0^0$. The excitation characteristic of this line, on the author's plates, is definitely too high to be consistent with this classification. In this analysis the line λ 1383.19 has been chosen as this transition. It is the only strong line with the proper excitation characteristic in the predicted region. This gives 130702.1 for the term value of 9_0^0. This term value is confirmed by the presence of the lines corresponding to its combinations with the terms 10_1 and 27_1.

The analysis is further confirmed by the hyperfine structures observed for a number of the lines in Table II. The observed structures are mainly isotopic in origin. It is to be noted that the lines which show these structures, all of which have an over-all width of approximately one frequency unit, are classified as transitions from a configuration with two $6s$ electrons to a configuration with no $6s$ electrons. This behavior is consistent with the classification since Breit's theory of isotope shifts (2) for the heavy elements predicts large structures for such transitions.

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SECTION B

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CANADA

THE EFFICIENCY OF PACKINGS FOR LABORATORY DISTILLING COLUMNS[1]

BY MELVILLE J. MARSHALL[2], FORESTIER WALKER[3], AND DONALD H. BAKER[4]

Abstract

The efficiency of jack chain packings, with alcohol-water mixtures, increases by only 13.2% with decrease in the size of the chain links from No. 18 to No. 22, while a drop in capacity of 36.7% is noted. If all factors are taken into consideration, No. 18 jack chain is the most desirable of those studied. The efficiency of Lessing rings, 0.22 in. in diameter, is higher than that of any of the chains studied, but the capacity is much less than that of No. 18 chain, and only slightly better than that of No. 22 chain.

Introduction

The use in recent years of small packed distilling columns for laboratory distillation has resulted in the introduction of a number of very efficient packing materials. Of these various packings, jack chain is often preferred because of the facility with which it can be handled. However, little use has been made of sizes smaller than No. 18, although it is known that a decrease in size results in a higher efficiency. In the present investigation the writers studied the effect of chain size on the efficiency and capacity of the packing, in order to determine the possibility of utilizing the smaller chain sizes to advantage.

Theory

Peters (6) was the first to calculate the number of perfect plates in a packed column. He used an equation similar to that of Lewis (3; 8, p. 600), as follows:

$$x_{n+1} = \frac{y_n - (1 - O/V)x_c}{O/V} ,$$

where x_{n+1} is the mole fraction of the more volatile component in the liquid on the $n + 1$th plate, y_n is the mole fraction of the more volatile component in the vapor from the nth plate, x_c is the mole fraction of the more volatile component in the distillate, P is the number of moles of distillate withdrawn as product per unit time, O is the overflow from one plate to another down the column in moles per unit time, V is the number of moles of vapor per unit time passing up the column, O/V is called the reflux ratio.

By dividing the height of the column by the calculated number of perfect plates, Peters (6) obtained a value characteristic of the efficiency of the column, which he called "the height equivalent to a perfect plate" or the H.E.T.P. As the efficiency is really inversely proportional to such a number, it would be preferable to define the efficiency as the number of plates per foot or per metre.

The efficiency is not the only criterion of the desirability of a given packing. The capacity of the packing to carry an adequate flow of vapor up the column without flooding is almost of equal importance. It is evident that the maximum reflux ratio permissible for a given amount of product per unit time decreases with decrease in the capacity of the packing. This, in turn, means a decrease in separating power, as can be seen from the equation. It is important, therefore, to employ packings that possess the highest combined capacity and efficiency.

The capacity is usually measured in terms of the maximum volume of vapor per unit time passing unit cross section of the column without flooding. This quantity has the dimensions of a velocity, and is called the maximum vapor velocity. Peters (6) found, experimentally, that this maximum vapor velocity dropped off as a linear function of the reflux ratio, giving a minimum value at total reflux. In the present investigation the capacity of a packing is defined as the maximum vapor velocity attained at total reflux.

Experimental Details

For comparison with previous work done in this laboratory, a mixture of ethyl alcohol and water was chosen to test the column. Care was taken to prevent the composition of the distillate approaching too closely that of the constant boiling mixture, as the theoretical change in concentration per plate is very small in this region.
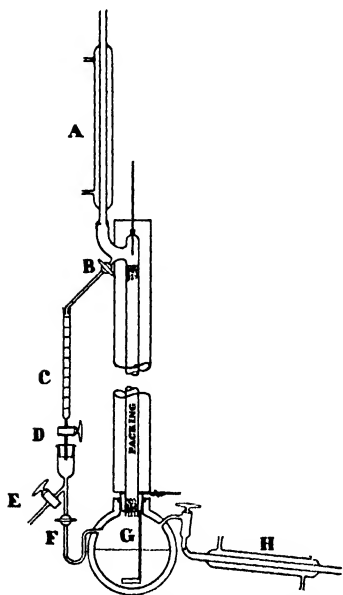
The experimental column, shown in Fig. 1, was constructed entirely of Pyrex glass, and was modeled somewhat after the laboratory column previously described by the senior writer (4). The boiling flask, G, was covered with asbestos cement to prevent undue heat loss. Heat was introduced by passing direct current through a nichrome wire immersed directly in the liquid. The rate of energy dissipation was measured in watts by means of an ammeter and a voltmeter. To obtain the amount of heat actually entering the column, the power in watts necessary to barely distil liquid out of the flask without the column was determined. This value was found to be 36

Fig 1. *Experimental column.*

watts or 8.6 cal. per second. The amount of energy entering the column per second with the vapor was obtained by subtracting this amount from the total power dissipated in the still. When converted to moles per second, this gives the vapor velocity, V.

The internal diameter of the column proper was 2.2 cm., and it was filled with packing to a height of 100 cm. It was heat insulated with steam pipe insulation, and correction was made for any possible heat loss by passing a current through a nichrome winding between the insulation and the glass column. Preliminary tests were made with no reflux down the column, and 40 watts was found to be necessary to just prevent condensation on the column walls. This value was verified by calculation of heat losses from the mean temperature difference and the conductivity of the insulation.

All the vapor passing the column was condensed in the reflux condenser, A. By adjustment of the glass stopcock B part of this reflux was passed back down the column and part was run into the burette, C. The rate at which the burette filled with product was determined by means of a stop watch. The condensate was then passed back to the boiling flask by opening stopcock D. A sample of the product was withdrawn for each run by closing stopcock F and opening E. A sample of the vapor in the boiling flask was withdrawn through the condenser II. The density of each of these samples was determined by means of a pycnometer, after which the samples were returned to the still. From these values the composition of the vapor entering, and that of the vapor leaving, the column were determined by reference to the density tables in the Smithsonian Physical Tables (6th ed.).

To obtain values for the capacity of the packings, the column was run at total reflux, and the heat input just necessary to cause flooding was determined. From the molal heat of vaporization the number of cubic centimetres of vapor at normal temperature and pressure passing unit cross section of the column could be obtained as a velocity in centimetres per second, The medium for most of these tests was alcohol (95% by weight), so the values obtained are practically those for the constant boiling mixture. In addition, some measurements were made with water, and some with alcohol and water mixtures of the same composition as those used in the efficiency determinations.

Results

The efficiency determinations for 0.22 in. Lessing rings, and Nos. 18, 20, and 22 single link brass jack chain are given in Table I. The method of calculation was exactly the same as that described by Marshall and Sutherland (5).

Table II contains the averages of the H.E.T.P. values of Table I, and the capacity of each packing expressed as a maximum vapor velocity. The maximum heat input at total reflux is included for comparison with the heat input data of Table I.

TABLE I

EFFICIENCY DETERMINATIONS

Reflux ratio	Heat input, watts	H.E.T.P., cm.
Lessing rings		
0.670	404	10.2
.812	408	10.0
.815	291	11.2
.816	388	11.1
.839	404	10.0
.857	360	10.0
.868	372	10.6
.868	170	10.0
No. 18 Single link jack chain		
0.802	294	12.0
.773	294	13.5
.805	404	14.0
.553	276	12.5
.841	353	13.0
.933	494	11.8
.860	386	12.5
.890	438	13.5
No. 20 Single link jack chain		
0.897	420	13.2
.854	360	11.3
.954	416	13.8
.818	281	13.1
.910	405	10.6
.894	364	12.5
.860	388	13.6
.843	440	13.8
.803	280	13.3
No. 22 Single link jack chain		
0.850	365	11.4
.855	360	11.9
.932	492	11.8
.900	403	10.6

A determination of the capacity of No. 18 chain, using water as the medium, gave a value of 215.2 cm. per sec. This very high value is due largely to the very small molecular volume of the liquid water. Similar determinations with No. 18 and No. 20 chains, using 15% alcohol in the still, which is about the concentration used in obtaining the efficiencies, gave results approximately 5% higher than those for 95% alcohol. This is explained by the fact that, at total reflux, the alcohol concentration at the top of the column is greater than 90%, even when that in the boiling flask is as low as 15%. As the capacity of the packing varies throughout the length of the column owing to variation in the composition of the reflux, it is evident that the capacity of the column as a whole is limited to the minimum capacity anywhere in the column.

The capacity of a column is also limited by the size of the condenser employed. In the present work, an ordinary Liebig condenser, made by the Corning Glass Co., was found to flood at 598 watts. To handle the highest rates of distillation it was necessary to replace the Liebig condenser with one of larger internal diameter. This point should be given some consideration when reflux columns for general laboratory purposes are designed.

TABLE II

AVERAGES OF H.E.T.P. VALUES OF TABLE I, AND CAPACITY OF EACH PACKING

Packing	H.E.T.P., cm.	Plates per metre	Max. heat input at total reflux, watts	Max. vapor velocity, cm./sec., 95% alcohol
No. 18 chain	12.9	7.75	709	104.5
No. 20 chain	12.8	7.81	667	98.3
No. 22 chain	11.4	8.77	449	66.2
Lessing rings	10.4	9.62	465	68.6

It is evident from Table II that no great gain in efficiency can be attained by decreasing the size of the chain from No. 18 to No. 22. Since a link of the No. 18 chain measures 6.3 mm. in width, compared with only 3.3 mm. for the No. 22 chain, the writers expected a greater increase in efficiency than was actually obtained. This small increase in efficiency, in view of the much larger decrease in capacity, the greater weight in the column, and the higher cost of No. 22 chain, hardly justifies the use of this chain for ordinary distillation. There seems to be no great advantage in using No. 20 chain, in view of the larger capacity of No. 18 chain and the small difference in their efficiencies. It would appear, then, that No. 18 chain is the most generally desirable of the three sizes. It is very probable, however, that a chain much lighter in construction than the conventional jack chain would give higher efficiencies in the smaller sizes.

No other efficiency values, with alcohol-water mixtures, are available for chain packings. For other mixtures, a number of values for the larger chain sizes can be found in the literature, particularly for benzene-carbon tetrachloride mixtures. No relative capacity measurements are available. Fenske, Quiggle and Tongberg (1, 2) have measured the efficiencies of chains from No. 16 to 20, but as these measurements have been distributed among a number of columns and mixtures, it has been found impossible, particularly in the absence of capacity data, to apply their results to the present problem. It is interesting to note, however, that the present efficiency values with alcohol-water mixtures are very close to their corresponding values with benzene-carbon tetrachloride and heptane-toluene mixtures, although in general the efficiency is found to vary with the nature of the mixture.

Comparison with Other Packings

Fewer data are available in the literature for capacity than for efficiency. Peters (6), calling the capacity of 0.25 in. hollow cylinders 100, estimated that the capacity of 0.25 in. solid spheres was about 70, and that of 0.25 in. solid cylinders, 54. There is no doubt from the writers' experience that the capacity of solid spheres or beads is much lower than that of hollow cylinders of approximately the same diameter. If the above estimate is combined with the present value for Lessing rings, a capacity of not more than 48 cm. per sec. would be obtained for spheres of the same diameter.

Efficiencies much higher than those of chain packings have been found for certain special packings. For instance, Fenske, Quiggle, and Tongberg (1, 2) have determined the efficiencies of a number of unusual types of packing, including one very efficient packing consisting of one-turn wire helices $\frac{1}{8}$ in. in diameter. Such a packing gave H.E.T.P. values roughly one-half those obtained with No. 18 chain.

When a glass packing must be employed the choice is rather limited. The efficiency of glass beads is good, but the capacity is low. Glass tubing about 7 mm. or less in diameter, cut into lengths approximately equal to the

diameter, will give good efficiency and capacity, provided that the walls of the tubing are quite thin. It is evident that thick walls would give a smaller free volume and a lower capacity, approaching the properties of beads. Wilson, Parker and Laughlin (9) describe a method for producing glass helices similar to the wire helices of Fenske, Quiggle and Tongberg (1, 2) mentioned above. Roper, Wright, Ruhoff and Smith (7) give additional information regarding the fabrication of these helices.

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'HE VISCOSITY OF VINYL ACETATE[1]

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Abstract

The viscosity of monomeric vinyl acetate has been measured over a range of temperatures from 0° to 60° C. Two equations were obtained which represent the results. The empirical equation is $\eta = \dfrac{1.521}{(90 + t)^{1.25}}$, and a theoretical equation is given as $\eta(v)^{\frac{1}{3}} = 470 \times 10^{-6} e^{\frac{702}{T}}$. The characteristic frequency has been obtained from the relation $Nh\nu = \dfrac{RT}{\dfrac{1}{\mu} - 1}$, where μ is the ratio between the latent heat of evaporation and the heat of cohesion. ν was found to be 2.17×10^{12}.

Experimental

The measurements were made with a Pyrex viscosimeter of the Washburn and Williams (14) type. It had the following approximate dimensions— radius of capillary, 0.025 cm.; length of capillary, 19.5 cm. The volume of the upper bulb was 9.97 cc. A 50 cc. pipette was used for filling the viscosimeter. A thermometer, reading to 0.1° C., was calibrated in purified boiling benzene, acetone, and water, and in crushed ice, and all necessary corrections for barometric pressure and exposed stem were made.

The temperature of the water bath, which had a glass front, was controlled by means of a toluene regulator, and the bath was thoroughly stirred. The viscosimeter was so supported in the bath that when removed it could be replaced in a vertical position. On the average, the temperature could be controlled to within 0.002–0.003° C. The viscosimeter was always filled by means of the same 50 cc. pipette. The time of flow was measured by a stop clock which was wound up tightly prior to the measurement of the time interval. It was frequently compared with a master electric clock, and no error beyond the personal error could be detected. The viscosimeter was, before each experiment, carefully cleaned with a cleaning solution, washed with distilled water and dried by means of a current of filtered air.

Calibration of the Viscosimeter

Benzene, carbon tetrachloride, water, and acetone were used in calibrating the viscosimeter. Benzene was first shaken with successive portions of concentrated sulphuric acid, washed with distilled water and shaken with mercury. The mixture was filtered, dried over calcium chloride and sodium, distilled and twice fractionally crystallized.

A sample of Merck's reagent carbon tetrachloride was used without further purification.

Water was purified by distilling distilled water from an acid (sulphuric) permanganate solution, and then from an alkaline permanganate solution. It was kept in a flask, the inside of which was coated with paraffin.

Acetone was purified by the method of Shipsey and Werner (12), *i.e.*, sodium iodide was dissolved in hot acetone and allowed to crystallize at $-8°$ C. The mother liquor was poured off and the crystals of $NaI \cdot C_3H_6O$ were dried by suction. The acetone was gently distilled off and dried for several days over phosphorus pentoxide.

Table I gives the results of the calibration of the viscosimeter.

TABLE I

CALIBRATION OF THE VISCOSIMETER

Liquid	Temp., °C.	$\eta \times 10^6$	$K \times 10^{-7}$	% Deviation from mean
Benzene	6.88	8007 (7)	204.2	0.30
		7972 (8)	203.3	−0.15
	20.00	6490 (7)	204.3	0.35
		6475 (8)	203.8	0.10
	39.99	4913 (7)	202.7	−0.45
		4923 (8)	203.1	−0.25
Water	5.51	14850 (7)	202.5	−0.55
		14953 (8)	203.9	0.15
	20.00	10005 (7)	203.8	0.10
		10087 (8)	205.4	0.90
		10050 (3)	204.7	0.55
	40.00	6525 (7)	203.2	−0.20
		6536 (8)	203.5	−0.05
		6560 (3)	204.2	0.30
Carbon tetrachloride	22.28	9388 (8)	203.4	−0.05
Acetone	20.00	3225 (7)	201.9	−0.85
		3250 (4)	203.5	−0.05
		Mean	203.6	±0.30

NOTE:—*The reference numbers in Column 3 refer to the source of the data. The values preceding reference No. 7 are from Thorpe and Roger, as given by Hatschek.*

In obtaining some of the results another viscosimeter was used. It was calibrated at five temperatures with benzene. The value of K was $(201.3 \pm 0.1) \times 10^{-7}$.

Purification of Vinyl Acetate

The vinyl acetate* used in these measurements contained a small amount of copper acetate, as a polymerization inhibitor, and traces of acetaldehyde and acetic acid. It was purified by two methods:— (i) by simple distillation

* *Supplied by Shawinigan Chemicals Limited.*

through a long spiral column and collection of the middle portion of the distillate, which was dried over calcium chloride and filtered; (ii) by treatment with dilute 0.1 N sodium hydroxide solution, washing with water, drying with calcium chloride and redistilling. No difference was found in the viscosity of the samples within the limits of experimental error.

Andrade (1, 2) has investigated the variation of viscosity with temperature and has arrived at the following relation, $\eta v^{\frac{1}{3}} = A e^{\frac{c}{vT}}$, where η is the viscosity; v, the specific volume at temperature T; A, a constant involving frequency of vibration, molecular dimensions and distribution of molecular field energy; c, a constant, proportional to about 1/10 of the total internal energy as derived from Van der Waal's equation. A was found to be 470×10^{-6} and $c = 702$, for vinyl acetate. The values for v were obtained from the data of Morrison and Shaw (11); and Green, Marsden and Cuthbertson (6).

The values for the viscosity of vinyl acetate at temperatures between 0 and 60° C. are given in Table II and shown graphically in Figs. 1 and 2.

TABLE II

VISCOSITY VALUES—(*a*) EXPERIMENTAL; (*b*) THEORETICAL

Temp., °C.	(a) Viscosity, poises	Fluidity	(b) Viscosity, poises*	% error $100 \frac{(\eta_{obs.} - \eta_{calc.})}{\eta_{obs.}}$
0.10	0.005472	182.8	0.005432	0.7
2.70	0.005278	189.5	0.005256	0.4
4.82	0.005122	195.3	0.005117	0.1
8.42	0.004891	204.5	0.004896	−0.1
**11.23	0.004723	211.8	0.004732	−0.2
11.60	0.004707	212.5	0.004714	−0.1
13.33	0.004616	216.7	0.004616	0.0
**15.15	0.004509	221.9	0.004518	−0.2
†17.30	0.004404	227.1	0.004408	−0.1
19.40	0.004305	232.4	0.004303	0.0
**19.98	0.004269	234.5	0.004276	−0.2
21.10	0.004221	237.0	0.004222	0.0
†21.60	0.004200	238.2	0.004202	0.0
28.40	0.003900	256.7	0.003898	0.0
34.00	0.003688	271.3	0.003676	0.3
35.80	0.003612	277.1	0.003608	0.1
†40.70	0.003449	289.7	0.003435	0.4
49.87	0.003166	316.1	0.003144	0.7
††60.00	0.002922	342.5	0.002867	2.0

* *Values obtained from the formula* $\eta v^{\frac{1}{3}} = A e^{\frac{v}{vT}}$, *where* $A = 470 \times 10^{-6}$ *and* $c = 702$.

** *Washed with water and dried over calcium chloride.*

† *Purified by treatment with sodium hydroxide.*

†† *This sample probably polymerized slightly.*

Those that are not marked were purified by simple distillation.

The viscosities calculated from the formula and the percentage errors calculated from $100 \frac{(\eta_{obs.} - \eta_{calc.})}{\eta_{obs.}}$ are included in Table II, Columns 4 and 5.
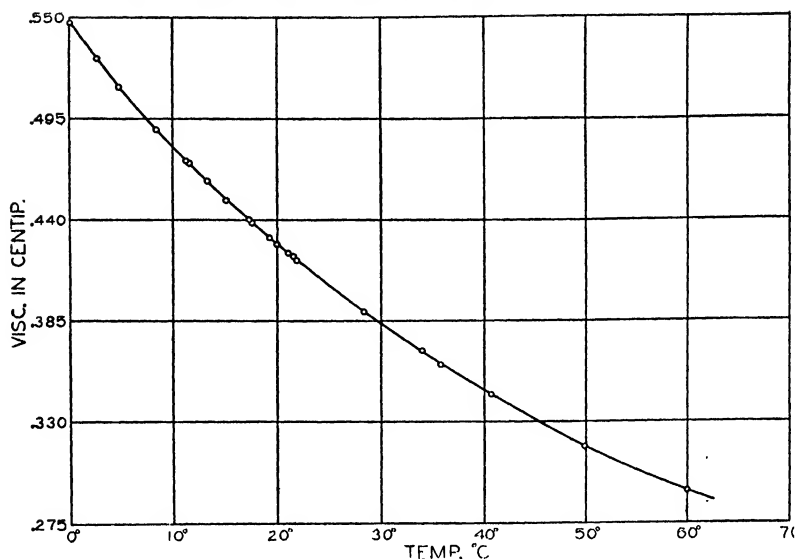
FIG. 1.   *Viscosity in centipoises plotted against temperature.*
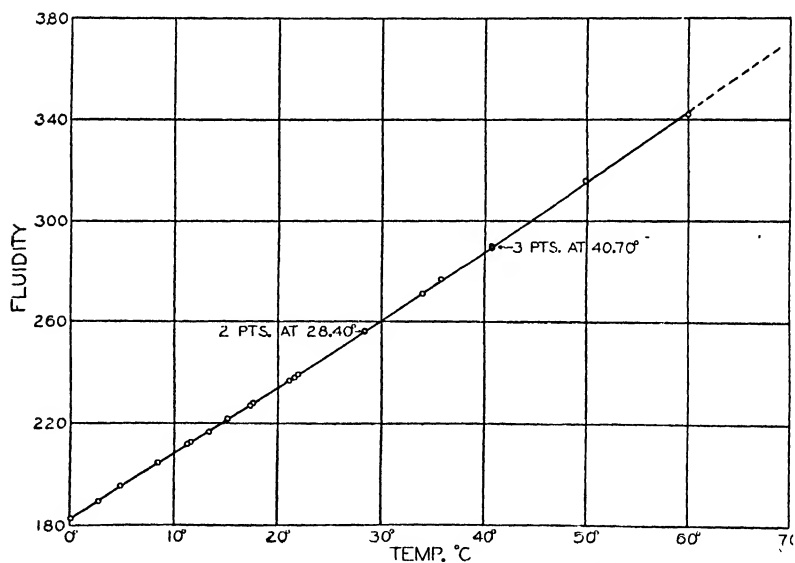
FIG. 2.   *Curve showing approximate proportionality between fluidity and temperature.*

For convenience, an empirical formula has also been derived of the form $\eta = \dfrac{1.521}{(90 + t)^{1.25}}$, where t is the temperature in ° C.   The equation represents the experimental data to an accuracy of 0.2%.

Drucker (5) has pointed out the relation $\log 1/\eta = \rho + \mu \log p$, where $1/\eta$ = fluidity, μ = ratio of the heat of vaporization and cohesion, and

p = vapor pressure in mm. of mercury (9, 10). On plotting log $1/\eta$ against log p, a straight line is obtained whose slope, is $\mu = 0.231$. The characteristic frequency, ν, is given by $Nh\nu\left(\dfrac{1}{\mu} - 1\right) = RT$, where N, h and R have their usual significance and $T = 345.5°$ A. (6, 9, 11). $\nu = 2.17 \times 10^{12}$.

The results from which μ may be obtained are given in Table III.

TABLE III

Temp., °C.	Log $1/\eta$	Log p, mm.	Temp., °C.	Log $1/\eta$	Log p, mm.
2.70	2.277	1.560	35.80	2.442	2.267
11.23	2.326	1.764	40.70	2.463	2.358
15.15	2.346	1.850	49 87	2.499	2.521
19.98	2.370	1.952	60.00	2.534	2.690
28.40	2.409	2.125			

Discussion

An attempt has been made to obtain a representative calibration constant K for the viscosimeter, by using four liquids and averaging the viscosity values given by different observers for the same temperature. From the results presented it appears that benzene may be used with some degree of certainty.

It has been anticipated that the viscosity of vinyl acetate might have been affected by the method of purification (13, p. 49), which exerts a profound influence on the rate of polymerization. Such however does not seem to be the case.

Staudinger (13, p. 49) gives as the viscosity of monomeric vinyl acetate at 20° C. the value 0.00421 as compared with 0.00427 obtained by the writers and a value of 0.00432 given by Morrison and Shaw (11). For purposes of purification the vinyl acetate was steam distilled and shaken with sodium hydroxide solution. It was found by the writers that unless very dilute sodium hydroxide solutions were used, resins were formed owing to the fact that the vinyl alcohol is rapidly changed to acetaldehyde and gives aldehyde resins.

Andrade's relation between viscosity and temperature has been found very satisfactory. The interesting aspect of the equation is that the problem is approached from the point of view of the solid state of aggregation.

A linear relation between the logarithms of the vapor pressure and fluidity as pointed out by Drucker seems justified.

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SORPTION OF WATER AND ALCOHOL VAPORS BY CELLULOSE[1]

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Abstract

Measurements were made of the amount of water vapor sorbed by beaten and unbeaten samples of kraft, unbleached sulphite and bleached sulphite wood pulps at relative vapor pressures ranging from 0 to 100%. Beating of the pulp made practically no difference to the degree of sorption at any relative vapor pressure. This indicated that beating caused no change in the hydration of the cellulose. Measurements were made of the sorption of methyl alcohol vapor by bleached sulphite, kraft and groundwood, and of the sorption of propyl alcohol vapor by bleached sulphite and cotton, all previously wetted with water and then dried. After sorption of alcohol, evacuation at room temperatures did not completely remove the alcohol. Measurements were also made of sorption of propyl alcohol by bleached sulphite and by cotton which had been dewatered by washing with propyl alcohol. The shape of the sorption curve was different for these samples, and the residual alcohol after evacuation was less. After a sample of cotton had been dried over phosphorus pentoxide in vacuo for a long period it was found to hold 0.35% of water by weight which could be removed by heating the cellulose to 100° C. This was regained from the pentoxide on cooling the cellulose.

The data are explained on the hypothesis that the crystalline submicroscopic elements of the cellulose structure are drawn together by internal tensile forces during the evaporation of the sorbed liquid, and that bonding between these elements may take place by the growing together of the crystal elements, leaving the structure internally stressed. On absorption, dissolution of these bondings takes place and the stresses are relieved as liquid enters the structure.

Introduction and Summary

In the making of paper the main phenomenon is the adhesion which unites cellulose fibres when, having been thoroughly wetted with water, they are allowed to dry in contact with one another. The effect of water on cellulose is almost unique in that practically no other liquid is able to substitute for water in bringing about the important phenomena on which depend most of the uses of cellulose. It was the purpose of these studies to attempt to obtain a better understanding of the mechanism of the interaction of water and cellulose by comparing such interactions with corresponding interactions where cellulose and alcohols were involved.

Previous study of the water vapor pressure over beaten and unbeaten cellulose pulp showed that, within the limits of experimental error, there was no difference in the vapor pressures. This indicated that beating caused no change in the degree to which water was bound to cellulose. In the first part of the present work the same ground was covered in a manner essentially the same as before but with a more refined technique. The results show no reason for altering the earlier conclusion.

The second portion of experimental work deals with the sorption of methyl alcohol vapor by papermaking pulps. The pulps used were groundwood, kraft and bleached sulphite, representative of uncooked wood, incompletely purified wood cellulose and highly purified wood cellulose. The amount of alcohol sorbed by the groundwood was greatest and by the bleached sulphite was least, but the general shape of the sorption curves was the same in all cases. The degree of sorption varied in each case according to the previous history of the sample. With the dried pulp there seemed to be some reluctance in regard to the taking up of alcohol until a moderate vapor pressure was reached, then the rate of sorption increased rapidly and followed a curve similar to that obtained in experiments with water vapor. On desorption to zero vapor pressure, the samples retained an appreciable amount of alcohol which was not removed by continued pumping. Curves of repeated adsorption showed a greater degree of pickup, and it was only after the third adsorption that the results were repeatable. In all cases a residue of alcohol remained in the samples at zero vapor pressure. The amount of alcohol sorbed was greater than the amount of water which similar samples sorb at the same relative vapor pressure when that pressure was low, but the reverse was the case at higher relative vapor pressures. The degree of hysteresis between adsorption and desorption was greater for alcohol than for water.

It is questionable what comparisons should be made to deduce the mechanism involved in these sorptions. If sorption is a matter of a layer of the liquid or highly condensed vapor adhering to all available surfaces, the basis of comparison should be volume sorbed against relative vapor pressure. If it is a matter of filling capillary passages, then the basis of comparison should be volume sorbed against capillary radius calculated from the lowered vapor pressure. But if, as will appear, sorption is a matter of release of strains controlled by internal liquid tension, then comparison should be made on the basis of volume sorbed against internal liquid tension calculated from the lowering of the vapor pressure. Comparison of the sorption of water and of alcohol on bleached sulphite pulp was made in each of these ways. Only the last comparison appeared to be of value. It indicated that the controlling factor in desorption was the drawing together of the fibre structure (shrinkage) under the influence of the internal liquid tension, and that the reverse action, modified by the effects of bonding, was effective on adsorption. According to this conception the residual alcohol is explained as being due to the limitation imposed by the obtainable internal tension, which is much lower with alcohol than with water.

The series of similar determinations with vapor of *n*-propyl alcohol was made chiefly for confirmation of this conception, in case it might be based on chance coincidence of the two sets of curves. The cellulose samples used were (i) bleached sulphite pulp as in the previous series, and (ii) a sample of cotton purified by boiling in dilute (1%) caustic soda solution. Two series of determinations were made with each of these materials. In the first, the cellulose samples were washed well with distilled water and were dried in

the apparatus before any alcohol was admitted. These will be designated "water washed". In the second series, the samples were washed with distilled water, and the water was removed as completely as possible by repeated washing with the alcohol. The samples were put into the apparatus while still containing liquid alcohol. These will be designated "alcohol washed".

The water washed samples behaved qualitatively in the same manner as did the samples similarly prepared in methyl alcohol. Quantitatively the sorption of n-propyl alcohol differed from the sorption of methyl alcohol much as the latter did from that of water. The reluctance to sorb the first portion of alcohol was more marked, the amount retained at zero pressure was greater, and the amount sorbed was greater at low vapor pressure and less at high vapor pressure. When the results were plotted on the basis of volume sorbed against internal tension, the points lay close enough to the equivalent data for methyl alcohol and for water to support the hypothesis that the internal tension modified by bonding was the governing factor in this sorption.

The alcohol washed samples were used because it was hoped that by removing the water in this way it would be possible to avoid or at least minimize the formation of the bonds which form on normal drying from water.

The phenomena of sorption of water and of alcohols on cellulose as shown by this work may be pictured as follows. The cellulose fibres in the plant constitute a structure which, though firmly united at various points, is yet rather open. In the plant, the spaces between the solid elements is filled with water and the structure is without strain. On removal of this water by evaporation the solid elements are drawn closer together by the internal tensile forces in the liquid, the deformation producing strains and corresponding stresses in the solid structure. Where the solid elements are drawn together sufficiently close, bonding may take place by crystallization so that these elements are united in the strained position, thus keeping the structure deformed after removal of the water If water is allowed to return to the structure the reverse occurs, bonds are loosened and the structure may approach the original, unstrained condition, to a degree determined by the amount of adsorbed water. But, because of the bonding, the amount of water picked up by adsorption at any definite vapor pressure will be less than that held at the same vapor pressure during desorption. As far as the bonding conception is concerned this is the same as that advanced by Urquhart (11), though in the present work it is expressed somewhat differently because of the concept of the action of the internal tensile forces of the liquid. In the case of alcohols the action is modified by the lower solubility of the carbohydrate units, so that the number of bonds formed or loosened is much less. Two conditions may exist. (i) If the fibre is first wetted with water and then dried, many of the bonds formed during this drying are not loosened by sorption of alcohol. (ii) If water is displaced by alcohol without drying, few bonds are formed. Moreover, the maximum degree of internal tension which alcohol can exert is much less than that

produced by water, with the consequence that zero vapor pressure is reached with considerable alcohol still held, much more than is the case with water. There is also a possibility that pockets may be formed in the structure during drying and that liquid may be trapped in these pockets.

Effect of Beating on Sorption of Water

The action of the papermaker's beater has never been explained to general satisfaction. Mechanically it is simple, the action being the bruising of the fibres when well wetted with water. But the drastic changes produced by this action have led to suppositions of some far reaching change in the fibre. On continued beating the paper stock becomes glutinous to the feel when wet and, when dried, it forms a hard, dense mass quite unlike that formed from unbeaten stock. The wet, beaten stock is jelly-like and like other gels, shrinks and hardens on drying. For this reason there is a widely held opinion that some process of hydration takes place in the beater. In fact, the term hydration is generally applied to the process.

It was to test the existence of such change of degree of hydration that the present experiments were undertaken. They were based on the argument that if beaten cellulose pulp is more highly hydrated than the same pulp when unbeaten, it should hold more water at the same vapor pressure. Hence, when the water held is the same in amount, the more highly hydrated pulp should show a lower vapor pressure. Experiments along similar lines by Campbell and Pidgeon (4, p. 74) have shown that there was no difference in this respect produced by beating, and hence that beating caused no change in hydration. The present experiments were intended to verify this finding under more exact conditions.

Experimental

Apparatus

The apparatus employed was that shown in Fig. 1. For description this may be divided into two parts, that used to determine the amount of water held by the pulp sample, and that used to control the vapor pressure with which the sample was in equilibrium.

To determine the amount of water held by the sample it was suspended on a quartz spiral, A, the extension of which could be measured by a catheto-meter. Since the extensions of the spirals used were found to be directly proportional to the weights suspended, the amount of extension was at all times a measure of the total weight, and when compared with the extension produced by the dry sample, a measure of the proportion of water held by the sample was obtained. The spiral was supported in a light glass frame, B, which had at the bottom a ring, C, through which passed the straight quartz fibre to which the sample was attached. On this straight fibre was a small crosspiece, D, which, by engaging with the ring prevented undue extension of the spiral. This device permitted attaching to the spiral samples carrying several times their weight of water, without inpairment to the accuracy of the readings. As soon as the total load fell to that which could be safely

carried by the spiral, the crosspiece lifted clear of the ring and readings could be taken. It was essential that the wet sample should not touch the glass tube, since capillary forces would cause it to adhere. The frame and spiral were in turn suspended in a glass tube of which the lower half, containing the sample, was immersed in a constant temperature water bath.
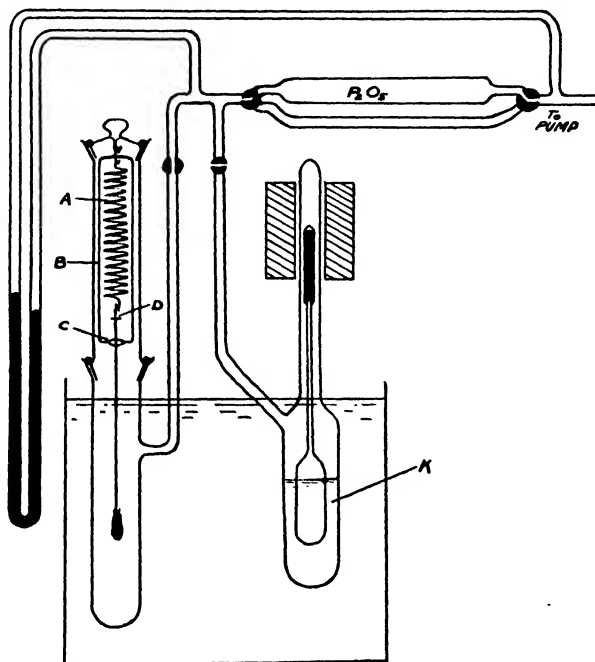
FIG. 1. *Apparatus for water sorption.*

For controlling the vapor pressure, the tube containing the sample was connected to a second tube, K, which contained sulphuric acid of strength appropriate to the pressure desired. The lower portion of this acid tube was also immersed in the same constant temperature water bath as the sample. During a test the acid was continually stirred by a glass float which was moved up and down by a solenoid outside the tube; the current in the solenoid was made and broken periodically through a switch operated by a windshield wiper. Between the acid tube and the tube containing the sample was placed a plug of glass wool to intercept any chance spray of acid. From the tube connecting the two, a side connection led directly or by way of a drying tube of phosphorus pentoxide to the vacuum pump. This side line was also connected to a mercury manometer, by means of which the vapor pressure in the system could be accurately determined.

In operation, the method was to attach to the spiral a sample of pulp containing a large excess of water, but which was of such a weight that the spiral would lift the bar from its supporting ring when the water content was reduced to about 40% of the dry weight of the pulp. The cell·was opened

to vacuum for a few moments, after which the stopcock leading to the pump was closed. After waiting some time to allow any air dissolved in the water of the sample to escape, the vacuum was again applied to remove this air. This process was repeated several times—until the McLeod gauge showed that the amount of residual air was negligible. Air was removed separately from the acid solution in the same manner. When both sample and acid were sufficiently free from air, the two compartments were connected by opening the stopcock, and the sample was allowed to come to equilibrium with the atmosphere conditioned by the acid.

The fibre materials used in this study were bleached sulphite, unbleached sulphite and kraft pulps, all of good commercial grades. Beating was done in the laboratory beater. The extent of the beating is shown by the decrease in the freeness test given in each table. The laboratory beater causes less cutting in proportion to "hydration" than does a large size mill beater.

Results are shown in Tables I, II and III. From these it will be seen that beating produced practically no change in the degree of hydration as measured in this way. The beaten pulps showed a slightly greater amount of water than the unbeaten. The formation of a slight amount of additional surface may be expected from the severe mechanical treatment, and this extra surface is consistent with the increased sorption shown in the data. On the other hand, equilibrium is reached much more slowly with the beaten pulps, and the difference, on the desorption cycle, is of the same order of magnitude as the experimental error. This explanation is hardly valid as the same difference appears on the adsorption cycle. The implications arising from this work are left for discussion later on in the paper.

TABLE I

SORPTION OF WATER VAPOR BY BLEACHED SULPHITE AT 27° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
1st Desorption (from saturation)			
0.689	11.8	11.7	1.01
0.417	7.3	7.0	1.04
1st Adsorption (from 0 R.v.p.)			
0.420	5.9	6.0	0.98
0.695	9.3	9.8	0.95
2nd Desorption (from 0.695 R.v.p.)			
0.425	6.5	6.3	1.03
2nd Adsorption (from 0 R.v.p.)			
0.426	5.9	5.9	1.00
0.690	9.5	9.3	1.02
0.900 (app.)	15.0	15.1	–
3rd Desorption (from about 0.90 R v.p.)			
0.688	10.6	11.0	0.96
0.420	7.0	7.3	0.96
		Average ratio	0.99

(a) *Freeness (Can. Stand.), 65 cc.*
(b) *Freeness (Can. Stand.), 748 cc.*

SORPTION OF METHYL ALCOHOL

Determinations of the sorption of methyl alcohol were made without any anticipations of what the results

would indicate, but in the hope that the phenomena connected with this close homologue of water would throw some light on the relations with water. These hopes appear to have been realized.

The pulps used were commercial samples of groundwood, kraft and bleached sulphite pulps. These received no preparation except thorough washing with distilled water to remove any water-soluble material. The samples were introduced into the cells while thoroughly wet. Dry weights were obtained by removing water by evacuation and absorption of vapor by phosphorus pentoxide. Only after being dried in this way were the samples exposed to alcohol vapor.

The control of alcohol vapor pressure by any method analogous to the use of acid solutions did not seem feasible. Therefore control was obtained by adding to or removing from the cells containing the samples small quantities of alcohol vapor. It was found by experience that stopcocks could not be relied upon when exposed to alcohol vapors for the weeks of exposure necessary. They were replaced by mercury seals in the vital part of the apparatus.

Fig. 2 is a diagram of the main features of the apparatus. The absorption

TABLE II
SORPTION OF WATER VAPOR BY KRAFT PULP AT 20° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
1st Desorption (from saturation)			
0.960	34.0	31.6	1.07
0.701	13.8	13.3	1.04
0.623	11.8	11.8	1.00
0.412	8.3	8.0	1.04
0.272	6.6	6.2	1.06
0.177	4.9	4.7	1.04
1st Adsorption (from 0 R.v.p.)			
0.156	3.9	3.7	1.05
0.274	5.0	4.9	1.02
0.402	6.7	6.8	1.02
0.610	9.8	9.1	1.09
0.692	11.5	11.2	1.03
0.949	22.8	21.6	1.05
2nd Desorption (from 0.949 R.v.p.)			
0.690	13.2	12.4	1.06
0.630	11.5	11.0	1.05
0.440	8.4	8.1	1.04
0.256	6.2	6.0	1.03
0.150	4.7	4.5	1.04
2nd Adsorption (from 0 R.v.p.)			
0.148	4.1	3.9	1.05
0.260	5.3	5.1	1.04
0.400	7.0	6.4	1.09
0.610	9.6	8.9	1.08
0.690	11.3	10.3	1.10
0.942	22.4	21.7	1.03
	Average ratio		1.05

(a) Freeness (Can. Stand.), 80 cc.
(b) Freeness (Can. Stand.), 720 cc.

TABLE III
SORPTION OF WATER VAPOR BY UNBLEACHED SULPHITE AT 20° C.

Rel. vap. pressure	Sorption, per cent of dry weight		
	Beaten (a)	Unbeaten (b)	(a)/(b)
1st Desorption (from saturation)			
0.947	33.6	31.3	1.07
0.836	20.2	19.5	1.03
0.690	13.0	12.8	1.02
0.609	—	11.1	—
0.398	7.2	7.2	1.00
0.252	5.7	5.6	1.02
0.150	4.2	—	—
1st Adsorption (from 0 R.v.p.)			
0.151	3.5	3.2	1.09
0.252	4.5	4.4	1.02
0.410	6.3	5.9	1.07
0.608	9.1	8.9	1.02
0.690	10.5	10.2	1.03
0.837	14.5	14.1	1.03
2nd Desorption (from saturation)			
0.947	30.8	29.0	1:06
0.845	20.4	20.4	1.00
0.692	13.1	12.9	1.02
	Average ratio		1.05

(a) Freeness (Can. Stand.), 54 cc.
(b) Freeness (Can. Stand.), 670 cc.

cell with its spiral balance and sample is shown at *A*. Three of these cells were connected to one header. The stock supply of purified alcohol was contained in the bulb *B*. The mercury traps for controlling the admittance
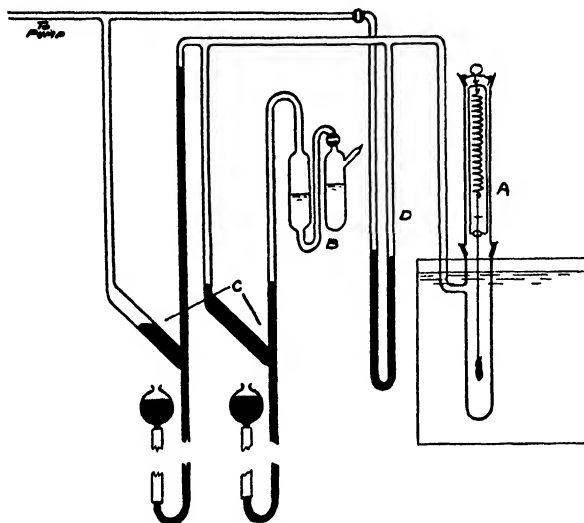
Fig. 2. *Apparatus for alcohol sorption.*

and removal of alcohol vapor are shown at *C*. The vapor pressure was measured by means of the mercury manometer, *D*, which was read with a cathetometer.

The alcohol was a good grade of synthetic methanol-which was redistilled and dried with metallic calcium, then sealed into the apparatus and twice distilled in vacuum at room temperature. Only the middle portion was used. When finally distilled it was received into the bulb, *B*, which was then closed off.

The results of these determinations are set forth in Table IV and in Figs. 3, 4 and 5. It will be noticed at once that there is evidence of a reluctance for the dry samples of the sulphite and kraft pulps to take up the first portions of alcohol. This is not shown by the groundwood. The first adsorption curve was followed up to a relative vapor pressure of 52.5% of saturation, at which time the amount of alcohol sorbed by the three pulps was—bleached sulphite, 7.05, kraft 8.58 and groundwood 11.50%. At this stage the pressure was reduced to zero without intermediate readings in order to remove any residual air, which, according to some investigators, notably McGavack and Patrick (8), is responsible for hysteresis between adsorption and desorption. On reducing the pressure to zero it was found that appreciable quantities of alcohol were retained in spite of the fact that pumping was carried out with a good mercury vapor pump for seven days. The amounts so retained were 1.98% on bleached sulphite, 2.13% on kraft and 0.75% on groundwood. A second adsorption curve was carried right up to saturation as shown by the

TABLE IV

SORPTION OF METHYL ALCOHOL AT 20.0° C.

Rel. vap. pressure	CH₃OH sorbed, per cent of dry weight			Rel. vap. pressure	CH₃OH sorbed, per cent of dry weight		
	Bleached sulphite	Kraft	Ground-wood		Bleached sulphite	Kraft	Ground wood
1st Adsorption				*3rd Adsorption*—Concluded			
0.000	0.00	0.00	0.00	0 2720	5.62	8.59	9.45
0.013	0.27	0.51	2.47	0.3970	6.83	9.69	11.10
0.054	0.61	1 54	3.98	0.5080	7.88	11.15	12.80
0.139	1.65	3.96	6.01	0.6090	8.76	12.20	13.80
0.197	2.59	5.00	6.77	0.7240	10.60	14.50	16.50
0.256	4.24	5.80	7 52	0.8220	12.10	16.10	18.20
0.401	5 84	7.26	9.55	0 8740	13.40	18.00	20.20
0.525	7.05	8.58	11.50	0.9180	14.80	19.70	21.80
				0.9560	16.90	22.20	24.20
				1.0000	19.30	24.50	27.50
1st Desorption							
0.000	1.98	2.13	0.75	*3rd Desorption*			
				0.921	17.10	22.70	24.60
				0 843	15.60	20 60	22.40
2nd Adsorption				0.696	13.30	17.50	20.40
				0 572	11.20	15.30	17.50
0.081	3.03	4.40	4.62	0.449	9.75	13.50	15.90
0.226	4.68	6.30	7.42	0.363	8.65	12.00	14.50
0.396	5.94	7.63	9.45	0.269	7.38	10.30	12 50
0.516	6.83	8.66	10.75	0.178	6.27	9.32	11.30
0.642	8.15	10.10	12.68	0.145	5 67	8.36	10 20
0.740	9.62	11.70	14 40	0.087	4.73	7.20	8.38
0.826	10.80	13.30	16.10	0.064	4.14	6.60	7 73
0.888	13.20	16.50	18.90	0.046	3.69	5.95	6.97
0.961	16.60	21.20	23.20	0.030	3.36	5.50	6.23
1.000	22.90	27.00	32.60	0.008	2.64	4.03	4 30
				0.000	1.93	2.35	1 61
2nd Desorption							
				4th Adsorption			
0.961	19.20	24.90	25.50				
0.841	16.20	20.70	22.60	0.032	2.42	3.60	4.62
0.730	13.90	17.50	19.50	0.144	4.40	6.45	7.41
0.591	11.80	15.00	17.10	0.296	6.11	8.15	9.67
0.481	10.20	13.00	15.20	0.446	7.32	9.61	11.1
0.385	8.92	11.20	13.40	0.571	8.59	11.30	13.4
0.296	7.92	10.10	12.00	0.723	10.60	13.90	15.8
0.227	6.77	8.66	10.60				
0.148	5.56	7.34	8.81	*4th Desorption*			
0.085	4.51	6.16	7.41				
0.000	2.08	2.12	0.75	0.6160	10.10	13.10	15.40
				0.5040	9.30	12.00	14.50
3rd Adsorption				0.3670	8.09	10.50	12.90
				0 2350	6 88	9.03	11.50
0.0105	2.15	3 52	4.08	0.1710	5.94	7.86	9.78
0 0277	2.48	4.55	5.27	0.0985	5.01	6.75	8.60
0.0673	3.30	5.50	6.23	0.0714	4.30	5.94	7.20
0.1100	3.85	6.16	6.87				
0.1850	4.46	7.19	7.63				

appearance of condensed alcohol. In the case of groundwood the first part of this curve was not distinguishable from the previous curve. In the case of the bleached sulphite and the kraft the second adsorption curve joined the first at about the point where the first had been discontinued.

A second desorption curve was determined from saturation down to zero pressure. Hysteresis between adsorption and desorption was very evident, and the amount retained at zero pressure was practically identical with that found after the first desorption.

A third adsorption was carried out to saturation and back to zero pressure. The adsorption curve ran above the previous one in all cases. The desorption curve was higher for the groundwood and the kraft, but was identical in the case of the bleached sulphite, except for a short

FIG. 3. *Sorption of methyl alcohol by bleached sulphite.*
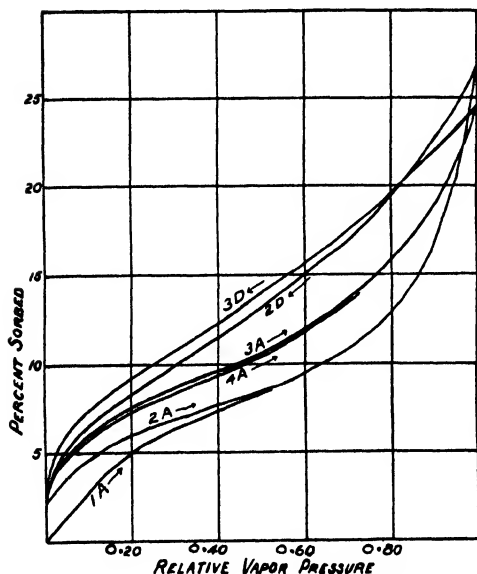
FIG. 4. *Sorption of methyl alcohol by kraft pulp.*
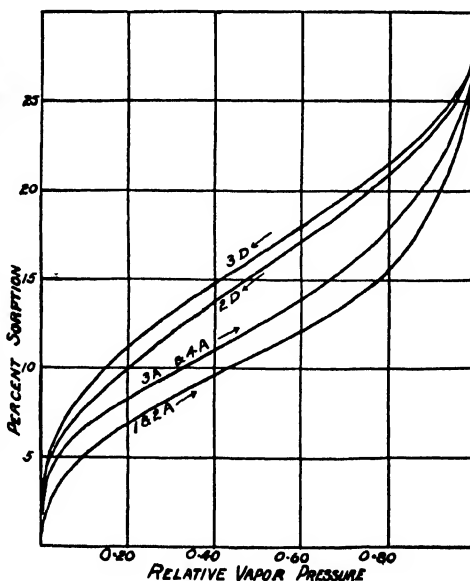
FIG. 5. *Sorption of methyl alcohol by groundwood pulp.*

portion near saturation where the difference in the amount of alcohol condensed on the sample evidently had an influence. The amount of residual alcohol at zero pressure was nearly the same as before in the case of the bleached sulphite, slightly higher for the kraft and nearly 1% higher for the groundwood.

A fourth adsorption was carried to 72% relative vapor pressure, over which range it followed practically the same course as the third adsorption. The desorption curve from this point gradually approached and finally joined the previous ones.

Further comment on these results will be found in the discussion.

SORPTION OF PROPYL ALCOHOL

After a study of the results of the sorption of methyl alcohol, it was decided to confine the experiments with propyl alcohol to the purer forms of cellulose. The samples used were bleached sulphite and cotton. The bleached sulphite was not treated in any way beyond a thorough washing in distilled water. The cotton was purified by repeated boiling in 1.0% caustic soda solution, followed by washing with distilled water (repeated seven times), then with dilute acetic acid and again with distilled water. Sorption by these materials was studied with the samples in two different original conditions. One set was put into the apparatus, wetted with water and this water was then removed by evaporation. In the case of the other set, substantially all the water was removed by long washing with alcohol without intermediate drying. The samples were put in the apparatus while still wet with the alcohol.

The alcohol used was supplied as being chemically pure *n*-propyl alcohol, but was further purified by drying with metallic calcium and twice distilling under vacuum, the final distillation being that into the storage bulb of the apparatus. This treatment should suffice to remove water and the most volatile impurities from the sample, but it would not remove other alcohols such as isopropyl. The alcohol used probably did contain some isopropyl alcohol, as shown by the fact that the vapor pressure was 17.08 mm. at 20° C. as against 14.5 mm. as given by the International Critical Tables for *n*-propyl alcohol. Over a temperature range of 10 to 30° C. the vapor pressure curve of the writers' material showed a regular displacement from that given by the data in the tables. In the calculation of relative vapor pressures the writers' value of the saturated vapor pressure was used.

Sorption Measurements

In making sorption measurements the apparatus and the general technique were the same as in the case of methyl alcohol sorption. In both cases the apparatus was completely sealed and free from stopcocks. The McBain-Bakr quartz spiral balance was used to determine the amount of alcohol sorbed. In some preliminary runs considerable trouble was encountered at very low pressures because of the tendency for mercury to distil from the manometer and seals to the samples. In the determinations reported, this difficulty was minimized but not entirely avoided by making the determinations at a

temperature above room temperature and by the interposition of a trap containing gold leaf. In spite of this precaution there was a certain gain in weight by the samples when the system was under vacuum. This increase could be due only to condensation of mercury on the samples. On this account there is some uncertainty as to the true dry weights. However, this uncertainty is not serious.

In order that the cycle of operations may be understood, a brief account of the determinations will be given as well as the presentation of the results in tabular form.

Water Washed Samples

The water washed samples of bleached sulphite and of cotton were put into the apparatus with excess water on the samples. Air was removed by repeated short time exposures to vacuum so as to remove the air with as little removal of water as possible. Weight readings were started when the relative vapor pressure of the water was about 0.66, and were continued until dry weight was obtained. During this drying the samples were kept at 25° C., but final dry weight was obtained by application of high vacuum with the samples at 35° C. to prevent condensation of mercury.

When the samples were dry, the temperature was again set at 25° C., alcohol vapor was admitted in successive small amounts, and the samples were held in each of these atmospheres until there was no apparent change in weight. The increase in weight was very slight until the vapor pressure of alcohol was above 50% of saturation, after which it mounted with comparative rapidity. This part of the data is not entirely satisfactory, as the greatest increase in weight took place during two weeks when no observations were made. It is accordingly uncertain whether the earlier low values of sorption were really due to small take-up at equilibrium, or were due to a very slow approach to equilibrium values not really reached. In view of similar behavior (at a lower vapor pressure) with methyl alcohol, it is thought that these low values were real. This adsorption cycle was continued up to the point where the samples were in contact with saturated vapor and some liquid alcohol had condensed in the cells containing the samples.

Following this adsorption, desorption points were determined, at 25° C., by removing successive small portions of alcohol vapor and waiting until equilibrium was reached. This desorption was continued until there was no measurable vapor pressure, and the samples had been subjected to high vacuum (mercury diffusion pump) for 10 days. During the last six days of this experiment the temperature was raised to 30° C. but no change in weight occurred.

A second adsorption curve was then determined in the same manner as before, but at 20° C. This was followed by a second desorption, which, because of the temperature of the water supply, was run at 26° C.

The results of the determinations on these water washed samples are given in Table V and Figs. 6 and 7.

TABLE V

SORPTION OF PROPYL ALCOHOL VAPOR BY WATER WASHED SULPHITE AND BY
COTTON CELLULOSE

Rel. vap. pressure of alcohol	Per cent sorbed by		Rel. vap. pressure of alcohol	Per cent sorbed by	
	Sulphite	Cotton		Sulphite	Cotton
1st Adsorption, at 25° C.			*2nd Adsorption, at 20° C.*		
0.095	0.13	0.10	0.068	4.38	3.48
0.230	0.32	0.21	0.098	4.55	3.51
0.418	0.52	0.42	0.144	5.55	4.26
0.539	2.19	1.22	0.274	6.62	5.07
0.680	2.43	1.38	0.391	7.28	5.54
0.995	5.13	3.07	0.544	8.40	6.37
Saturation	11.9	8.3	0.675	9.10	6.63
			0.795	9.95	7.23
1st Desorption, at 25° C.			0.910	12.67	8.80
			0.940	14.51	10.06
			0.980	21.9	12.92
0.940	11.30	8.16	Saturation	35.7	20.6
0.830	10.72	7.78			
0.700	10.40	7.62			
0.565	10.02	7.37	*2nd Desorption, at 26° C.*		
0.472	9.85	7.26	0.932	21.10	14.79
0.424	9.57	7.05	0.788	12.45	8.97
0.348	9.08	6.84	0.688	12.06	8.81
0.276	8.50	6.45	0.532	11.35	8.42
0.254	8.15	6.04	0.424	10.99	8.16
0.230	7.91	5.88	0.348	10.15	7.59
0.184	7.74	5.75	0.280	9.64	7.25
0.161	7.47	5.54	0.208	8.85	6.63
0.151	6.93	5.18	0.132	7.85	5.90
0.115	6.70	4.97	0.088	7.15	5.51
0.080	6.20	4.63	0.068	6.46	4.97
0.0604	5.90	4.45	0.040	5.99	4.68
0.0425	5.14	3.90	0.036	5.56	4.37
0.0290	4.76	3.93	0.028	5.32	4.16
0.00	4.04	3.36	0	4.34	3.48

Alcohol Washed Samples

The alcohol washed samples were prepared as follows. Portions of the sulphite and cotton cellulose samples, prepared as described for water washed material, were taken, and, without drying, were diluted with alcohol. After several hours soaking, the larger portion of the now diluted alcohol was removed by gentle squeezing. Compensation was made for this loss by the addition of strong alcohol. The washing with alcohol was repeated many times, until the water content of the residual alcohol was estimated to be less than 2%. The samples, wet with an excess of this nearly pure alcohol, were then hung on the spirals and put in the cells.

Because of the uncertainty regarding the water content, the weights of the samples during the first evacuation, and the corresponding vapor pressures,
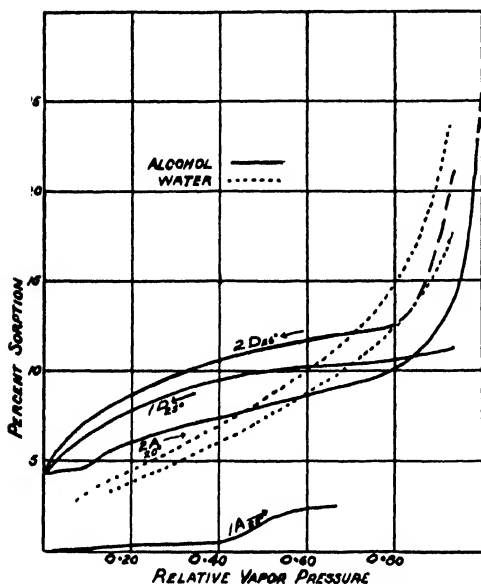
FIG. 6. *Sorption of propyl alcohol by bleached sulphite (water washed).*
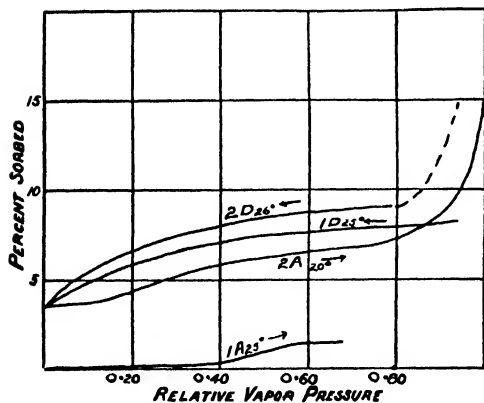
FIG. 7. *Sorption of propyl alcohol by cotton cellulose (water washed).*

are not recorded here. As the alcohol used had at 20° C. a vapor pressure of 17.08 mm. as compared with 17.53 mm. for water, it was considered that the small water content of the residual alcohol would not seriously affect the amount retained. A difficulty was experienced in obtaining the final weights in vacuum. On subjecting the samples to vacuum, the weights quickly reached a minimum and then started to increase. This increase was due to condensation of mercury on the samples when the room temperature or the temperature of mercury in the traps, etc., was above that of the bath. The extra weight picked up during this drying period was deducted from the total weight increase in the subsequent adsorption, and the balance considered to be alcohol.

One adsorption was carried to saturation at 20° C., followed by a desorption to vacuum dried weight, for which again the lowest weight reached was taken. There was a similar pickup of mercury at this stage of vacuum treatment for which allowance was made in subsequent treatment. This subsequent treatment consisted in repeated addition and evaporation of water vapor to remove residual alcohol not removed by vacuum. The loss of weight by this treatment was considered to be due to removal of alcohol.

Mercury Condensation

During the work the question arose as to whether the mercury that was picked up by the samples when under high vacuum was deposited as the result of condensation of mercury vapor, or whether it was actually sorbed. The following experiment was carried out, and it indicates that the process was one of condensation.

A sample of cotton cellulose was hung on a quartz spiral in a cell such as that used in the main work. Between this and a mercury reservoir there was interposed a coil of tubing such that it could be surrounded by a water bath which was kept at a temperature of about 3° C. by a flow of tap water. The mercury was at room temperature (about 25° C.), while the sample was at 20° C. The whole system was kept evacuated by means of a mercury diffusion pump. Under these conditions there was no increase in the weight of the sample in 20 days.

On stopping the supply of cold water to the intermediate cooling coil, the weight of the sample promptly increased, and in 40 days the extension was too great to be read by means of the cathetometer, *i.e.*, the quantity condensed was more than 27% of sample weight. Then the cooling was resumed, and it was found that the weight of the sample returned almost exactly to its original value although the temperature of the cooling coil was now about 14° C., which was the tap water temperature at this time.

The correction for weight of condensed mercury in obtaining the dry weight of pulp used is not altogether satisfactory. The manner in which this correction was made is as follows:—The first drying under vacuum gave a low total extension of 100.10 mm. for the sulphite cellulose. This is considered to be the "dry weight" of the sample plus residual alcohol not removed by vacuum. After the second vacuum drying, the sample contained both residual alcohol and condensed mercury. Treatment with water vapor reduced the weight by an amount represented by 2.38 mm. extension which is taken as the amount of residual alcohol. The assumption is then made that this same amount of residual alcohol was present when the first "vacuum dried weight" (100.10 mm. extension) was determined. The "dry weight" of the sample is then the difference between these two, *i.e.*, 97.72 mm. Just prior to the starting of the first adsorption, the sample had picked up mercury corresponding to 2.34 mm. In the presence of a considerable pressure of alcohol vapor none of this would be lost during the adsorption, so this amount (2.34 mm.) is deducted from these observed extensions in order to obtain the extensions due to sample plus alcohol during this period. During desorption, however, some of the condensed mercury might be lost by entrainment with the alcohol vapor evaporating from this sample. The low extension reached on evaporation was 101.90 mm. Allowing 100.10 mm. as a measure of the weight of sample plus residual alcohol, the condensed mercury present at this time was 1.80 mm. and an allowance of this amount was made throughout the desorption data. The difference of 0.54 mm. is considered as mercury lost by evaporation. Similar corrections were made for the cotton sample.

Errors involved in this adjustment are included in the values for high sorption. During the adsorption period the amount of mercury is likely to increase. During the desorption period it probably decreases as desorption proceeds, so that the values for sorbed alcohol in this series may be

slightly high. In addition to this allowance for mercury there is, of course, a slight uncertainty as to whether all the alcohol was removed by water. Error from this source is probably inappreciable.

The alternative to this is to consider that all mercury picked up on first vacuum drying remained on the samples throughout the desorption. This would lower the assumed dry weight by 0.54 mm. extension and increase the amounts in the adsorption series. It would make practically no change in the desorption series since the extensions attributed to sorbed alcohol would be the same as before. Only the dry weight on which percentages are based would be changed by about 0.6%.

The results of the determinations on the alcohol washed samples are given in Table VI and Figs. 8 and 9.

TABLE VI

SORPTION OF PROPYL ALCOHOL VAPOR BY ALCOHOL WASHED SULPHITE AND COTTON CELLULOSE

Rel. vap. pressure of alcohol	Per cent alcohol sorbed by		Rel. vap. pressure of alcohol	Per cent alcohol sorbed by	
	Sulphite	Cotton		Sulphite	Cotton
Adsorption at 20° C.			*Desorption at 26° C.*		
Vacuum dried*	2.44	1.13	0.918	—	30.54
0.014	3.01	2.26	0.849	18.62	13.08
0.046	3.78	3.14	0.785	17.31	12.48
0.103	5.16	4.23	0.672	15.98	11.76
0.241	6.69	5.47	0.593	15.12	11.31
0.379	8.04	6.45	0.522	13.67	10.43
0.518	9.68	7.58	0.460	·12.89	9.89
0.630	11.11	8.62	0.412	11.91	9.32
0.761	13.65	9.96	0.330	10.83	8.48
			0.279	10.19	8.03
0.890	22.18	18.10			
0.916	28.50	23.68	0.214	9.10	7.15
Saturated	—	31.58	0.174	8.49	6.63
			0.107	6.49	5.25
			0.067	5.63	4.48
			Vacuum dried†	2.44	1.13

Lowest weight. Mercury picked up before adsorption of alcohol, in per cent of weight of sample, on sulphite 2.40%, on cotton 1.92%.

†Lowest weight. Mercury on sample at this point, on sulphite 1.80%, on cotton 0.98%. Alcohol content taken as equal to weight lost on treating with water vapor.*

Effect of Temperature on Residual Alcohol

The effect of temperature on the amount of residual alcohol held by cellulose was examined at temperatures between 2° and 40° C.

Samples of sulphite and cotton cellulose were placed on spirals and dried over phosphorus pentoxide in high vacuum to a constant weight. Methyl alcohol vapor was next admitted until condensation in the cells was noted. Samples were kept in this vapor for two days at 2° C., and the alcohol vapor was pumped off until the sample weight was constant for two days. (Conden-

sation of mercury vapor was prevented by means of a cooled trap between the samples and the mercury diffusion pump.) The samples at this point showed alcohol sorption of 1.83% by the cotton and 2.18% by the sulphite. Increase of temperature caused a regular drop in this amount, so that at 40° C. the amounts retained were 0.58% by the cotton and 0.97% by the sulphite. This statement that the drop is a regular or a straight line relation must be qualified slightly, because, at about room temperature, there was an interval of about 4° in which no change of weight was noted. This break in what are otherwise straight lines is believed to be due to an experimental error.

FIG. 8.   *Sorption of propyl alcohol by bleached sulphite (alcohol washed).*

Effect of Temperature on Residual Water

The weight of the cellulose after it has been dried in vacuum over phosphorus pentoxide is usually taken as the dry weight. This is not an absolute value but is reproducible. The following experiment was made to determine the effect of temperature on the water retained in such "dry" cellulose.

A sample of cotton was hung on a spiral in a tube connected, by a side arm, to a bulb containing phosphorus pentoxide, and the whole thoroughly evacuated and sealed off from the pump.

FIG. 9.   *Sorption of propyl alcohol by cotton cellulose (alcohol washed).*

The extension of the spiral was then read. This gave the dry weight of the sample. This did not change over a period of several days. Then the lower end of the tube containing the sample was immersed in water at various temperatures, and the loss in weight determined at temperatures up to 100° C. (Table VII).

On lowering the temperature to that of the room the original dry weight was obtained. The experiment was repeated several times and can indicate

only that cellulose, when so dried, still retains water with a vapor pressure lower than that retained by phosphorus pentoxide.

TABLE VII

LOSS IN WEIGHT (ACCURATE TO LESS THAN 0.04%)

Temp. °C.	%
40	0.04
60	0.10
80	0.17
100	0.35

In another experiment this water was made apparent by using a large sample of cellulose in a bulb connected by a side arm to a capillary tube in which the vapor could be condensed by a carbon dioxide freezing mixture. The cellulose was dried by application of high vacuum and in the presence of phosphorus pentoxide for three weeks and then sealed off from the vacuum and drying bulb. On warming the bulb containing the cellulose and cooling the capillary in the freezing mixture, vapor condensed and the water froze in the capillary. The water was quickly adsorbed by the cellulose when allowed to thaw.

Discussion

In discussing these results it is difficult to distinguish at all points between what is proved and what is speculative. In the authors' opinion the phenomena are associated with the action of physical forces of surface tension and internal liquid tension combined with effects due to surface solubility of cellulose in the liquids concerned, all acting on an open but well bonded solid structure of cellulose. Of the existence of these forces of surface tension and internal liquid tension there is no doubt. There is also little doubt that cellulose consists of a well bonded structure of small units among which water and other liquids may be held. The surface solubility of cellulose, particularly the peculiar character of this solubility, is a much more speculative conception.

As the possibilities of internal liquid tension have not been drawn upon to any great extent in general explanations, and as liquids are not usually regarded as having tensile strength, something may be said about this phenomenon. Consider a capillary tube in which a liquid has risen by capillary action to some height, h cm. If the pressure of the liquid at the general surface level is taken as zero, then the liquid in the tube, being at a higher level, must be under a negative pressure, i.e., under tension. At points in the tube corresponding in elevation to the general liquid level, this tension is just balanced by the pressure due to the column of liquid above it. Consequently the tension at the top of the column is equal to the weight of the column. The tension may be calculated by either of two methods: (a) from the known surface tension of the liquid, together with the known diameter of the capillary tube; or, (b) from the reduction of the vapor pressure of the liquid at the top of the tube. Method (a) is merely the inverse of the usual method for determining surface tension from capillary rise. Method (b) depends on determining the tension at the top of a column of liquid of a height equal to the height of a column of vapor necessary to reach a definite

degree of pressure lowering. As this latter method requires no knowledge of the surface tension in extremely small capillaries or of the size of such capillaries, it is more generally applicable. The tension, P, may be calculated from the formula

$$P = \frac{195\ T\ \sigma\ \log\ (p_o/p)}{M}\ \text{kg. per sq. cm.,}$$

where, T is the absolute temperature, M is the molecular weight of the liquid when in the gaseous state, σ is the density of the liquid and p/p_o is the vapor pressure at the surface of the liquid in the capillary relative to the normal vapor pressure over a plane surface.

That cellulose has a structure of solid units bonded together in some way with open or potentially open spaces is evident from the X-ray observations by Katz (6), who concluded that, since cellulose swollen by water or salt solutions did not show any change of crystal structure, the water must be between the crystals and not in them. Botanical evidence also points to the same conclusion. The fibrillation or splitting of fibres evident as a result of paper mill beating is probably a manifestation of the same thing, though it may be, in part, a matter of crystal cleavage. That there is a considerable degree of bonding of the structure is evident from the fact that there is a well defined limit to the swelling in water. If there were no bonding to restrain it, the swelling would proceed to the point of complete dispersion of the units.

These two facts, a bonded but open network structure of solid cellulose units and the effects of the forces of surface and internal liquid tension, account for many of the phenomena of the sorption of vapors by cellulose, but do not so do completely. Something must be due, in addition, to the specific nature of the liquid concerned. In discussing the hysteresis between the adsorption and the desorption parts of the cycle of water sorption, Urquhart (10, 11, 12) points out that, in the plant, the cellulose is laid down in the presence of water and that much of this water is closely associated with the hydroxyl groups of the cellulose. On removal of the water, by drying, the affinities of the hydroxyl groups become satisfied with each other and so form bonds between parts of the structure which, before drying, were free. He considers that deformations brought about in this way are responsible for the internal stresses evident in dry cellulose.

According to our view the strains are brought about by the action of the liquid forces previously mentioned, but the dry material is held in the strained position by a bonding mechanism essentially the same as he postulates.

The work of Haworth (5), Stamm (9), and others leaves little doubt that the cellulose molecule is a long chain of 100 or more glucose anhydride units. Since glucose is quite soluble in water and short chains of similar character are also quite soluble in water, it seems reasonable to suppose that the insolubility of cellulose may be more apparent than real, in the sense that the units of the chain may be soluble though the chain itself is not. In a saturated solution of a substance such as sugar, having molecules of moderate

length, there is a continual process of solution and crystallization going on at the surface of any crystal of sugar in contact with the solution. The solution being saturated, the rates of these two processes are equal. In the case of cellulose, we conceive of the same being true with respect to the unit groups of the chain, but that the whole molecule can escape from the crystal only in the rare event of all its constituent units being simultaneously dissolved. Such a condition would permit of ready bonding by recrystallization even without very close contact, since individual cellulose molecules might become attached to more than one crystal. In liquids such as alcohols, which are not good solvents for sugars, the possibilities of forming such unions or of loosening any which have formed are much less. Such a condition may be described as one of "surface solution" or, if water is the solvent, as "surface hydration".

While the hypothesis of the mechanism of sorption by cellulose here advanced was evolved largely from these experiments, the discussion will be simpler if the hypothesis is presented first and the experimental findings then examined to see how they fit.

As Urquhart pointed out, cellulose is formed in the plant in the presence of excess water, and when first formed is without strain. In drying out, the water filling the spaces in the fibre, and even in the spaces between the fibres, exerts a tensile force drawing the whole together. Wherever this force is resisted by the rigidity of the structure, deformation of the structure necessarily results. The intensity of such force is surprisingly quite large. Two cylindrical fibres of 0.001 mm. diameter, in contact with each other, but with enough water to fill the "nip" between them, will be pulled together with a force of about one and a half atmospheres by surface tension alone. The intensity of the pressure over the very small area of actual contact will be many times this. If the structure is sufficiently rigid to withstand these stresses without its parts coming close enough to be bonded by recrystallization, then the water column will break leaving two independent cellulose surfaces. In general, this is what happens in a mass of fibres. A few bonds are probably formed between individual fibres when a mass of cotton dries from water, but such bonding is not extensive. However, if the diameters of the fibre units are reduced, as by the fibrillation mechanically brought about in beating, then the intensity of the tensile forces is greater and the rigidity of the fibre units is less, so that much more bonding results.

In an individual fibre there is a similar condition, intensified because the units are so much smaller. When loss of water proceeds so far that water begins to be evaporated from the exceedingly fine passages in the fibre wall, the internal liquid tension rises to high values. Even at 90% relative humidity it is equivalent to an external pressure of 142 atm. In rigid gels such as silica gel or charcoal the structure resists the deforming force for the most part and maintains its dimensions, but in non-rigid gels such force causes shrinkage in proportion to the volume of liquid lost by evaporation. Portions of the solid structure brought into contact by such deformations may become

bonded together by recrystallization if the liquid is one that can form such "surface solutions" as were earlier described. Such is the case with cellulose and water. In the case of rigid gels the liquid simply evaporates and leaves a corresponding volume of empty space. McGavack and Patrick (8) found that, in the case of silica gel, the volumes of all liquids sorbed were substantially the same, indicating that the capillary space available was the main factor in this case. Under such circumstances there should be no hysteresis between adsorption and desorption, and these investigators claim that no hysteresis is found when proper precautions are taken to avoid the presence of non-condensing gases. Their conclusions, even if valid for rigid gels, should not be extended to cover non-rigid gels such as cellulose.

When the alteration in properties of pulp brought about by the beating process is kept in mind, the data on water sorption of beaten and unbeaten pulps are seen to agree with these ideas. Since the only possible chemical reaction in the beater is one between cellulose and water, and, as this does not take place, as shown by the unaltered character of the vapor pressure curve, it follows that the changes effected by beating are purely physical. Moreover they must be physical on a scale involving units somewhat larger than those generally considered as colloidal and therefore within microscopic range. The fibrillation of the stock, as seen on microscopic examination, is of such a nature.

With the assumption that some form of bonding normally occurs when cellulose surfaces dry in actual contact with each other, the changed properties of paper stock brought about by beating are accounted for by such fibrillation, and the action of surface tension and internal liquid tension on the greatly increased external surface available for such bonding. This phase of the problem was discussed at length by Campbell (1, 2, 3) in earlier papers.

The sorption of alcohol vapors, according to the hypothesis outlined, will differ from that of water vapor chiefly because of (i) the difference in the degree to which bonding is affected, (ii) the much lower intensity of the surface tension, and (iii) lower internal tensile forces at similar relative vapor pressures.

As examples of different degrees of loosening of bonds uniting fibres in paper, the following tests may be cited. A sample of paper was tested under the usual paper testing conditions (70° F., 65% relative humidity) and also when wet with water, methyl alcohol, ethyl alcohol and propyl alcohol. The results are shown in Table VIII. (Tensile test.)

The destructive effect of water on the bonds formed between the fibres is evident, as is also the progressively smaller effect of wetting as higher alcohols are used.

Since the sorption phenomena with the alcohols seem to be of similar nature for the different cellulose samples, differing only in degree, it will suffice to consider only the bleached sulphite pulp since it was used with both methyl and propyl alcohols.

TABLE VIII

Wetting substance	Tension, kg.
Water	0.69
Methyl alcohol	2.32
Ethyl alcohol	4.63
Propyl alcohol	5.77
Dry	7.28

Considering first the water washed samples, *i.e.*, those that were first wetted with water and then dried, we note that on first adsorption there is a reluctance, on the part of the sample, to sorb alcohol until the vapor pressure rises considerably. This is much more marked with propyl than with methyl alcohol. In the case of the propyl alcohol, adsorption was only slight until the vapor was nearly saturated, and no exact values were obtained in this region. With methyl alcohol the sorption increased rapidly after the relative vapor pressure reached 0.20, and was nearly normal at a relative vapor pressure of 0.40. While there is some doubt as to whether these values represent true equilibria or only an exceedingly slow rate of pickup, they do accord with the general ideas of the relative loosening of bonds in the two liquids. It is to be expected that the bonds formed during the drying from water will be difficult to loosen in alcohol.

The first adsorption of methyl alcohol was carried to a relative vapor pressure of only 0.525, after which desorption to zero pressure was carried out without intermediate measurements. A second adsorption curve merged with the first about where the first was discontinued. This second adsorption was carried to saturation and a desorption curve from this point to zero pressure was obtained. A third adsorption curve to saturation was only slightly above the second, and a third desorption was identical with the second except for a short range near saturation, where values are probably influenced by the amount of liquid between fibres as well as by that in the cellulose structure itself. A fourth adsorption was identical with the third as far as it was carried (relative vapor pressure 0.723). From this point the desorption curve merged with the other two desorption curves at a relative vapor pressure of about 0.25.

If the third adsorption and desorption curves are taken as representing reproducible conditions, it is to be expected, according to our hypothesis, that, when volumes of sorbed liquid are plotted against internal liquid tension, the alcohol adsorption values should lie below the water adsorption values for the same reason that the water adsorption values lie below the desorption values, *viz.*, because fewer bonds are loosened. The data, plotted in this way in Fig. 10 show that this is the case.

On desorption, however, the bonds play a minor role, the main factor being the action of internal liquid tension drawing the structure together. The effect of bonding cannot be altogether

FIG. 10. *Sorption (by bleached sulphite) plotted against liquid tension.*

absent because, at saturation, alcohol does not cause a loosening of as many bonds as does water and consequently in this region a somewhat greater volume of water may be expected for the same internal stress. But over the greater part of the desorption curve the volumes of alcohol and of water should be the same for the same internal liquid tension. This is also found to be the case.

The propyl alcohol sorption cycles were not repeated as fully as were those of methyl alcohol. The first adsorption showed comparatively little pickup. A rather sudden rise at about a relative vapor pressure of 0.50 occurred when the apparatus was unattended for some time. This phenomenon may or may not be significant. However, not much alcohol was sorbed until the sample was wet with condensed liquid at saturation. After the first desorption curve was determined, a second adsorption was made which was quite different in character from the first. After a short initial lag, which was rather like that found in the first adsorption of methyl alcohol, the general form of the curve was similar to those previously found. A second desorption curve lay somewhat above the first. Unfortunately further work was impossible.

When the second adsorption curve for propyl alcohol was plotted as volume sorbed against internal liquid tension, it was found to be displaced from that of methyl alcohol in the same sense and to about the same degree as the latter curve was displaced from that of water. There is some uncertainty, however, about the lower end corresponding to the part where a lag in adsorption occurred. A possible explanation of this will be suggested later.

On desorption, by the same argument as advanced in the case of methyl alcohol, it is to be expected that internal liquid tension will be the governing factor. In accordance with this, the curves obtained by plotting volumes of water, methyl alcohol and propyl alcohol against internal tension are identical, within the range of experimental error.

The determinations with alcohol washed samples of cellulose were made to ascertain what would be the effect of eliminating the water formed bonds as far as possible. It was thought that the replacing of the water by alcohol without intermediate drying would leave the structure in much the same state of dispersion, with but a much diminished chance of forming new bonds as the liquid evaporated. The idea was much the same as that of Kistler (7), who replaced the water in several gels in this manner, and finally replaced the substitute liquid by air without allowing surface tension to come into play to compress the gel.

Since the bonding in the alcohol washed material is, presumably, less than that in the water washed, the structure should be less rigid and therefore more compressible. It should accordingly show a more rapid decrease of volume of sorbed liquid as the internal liquid tension is increased. Reference to Fig. 11 shows that this is the case.

On adsorption on the alcohol washed material, the release of bonds should approximate the release when water is absorbed by a water washed sample, because in each case the bonds are being loosened by the same liquid in which

they were formed. But in the alcohol washed sample the volume has been decreased in part by rearrangement of structure possible because of less rigid bonding. Hence, for the same volume of voids available for each liquid, there will be less stress in the cellulose structure tending to expansion. In consequence, at any value of the internal liquid tension there will be less volume of the liquid sorbed. Reference to Fig. 11 shows that this is also the case.

FIG. 11. *Sorption (by bleached sulphite–alcohol washed) plotted against liquid tension.*

The fact that alcohol is retained by all samples at zero vapor pressure, or at least at a pressure as low as could be produced by a good mercury diffusion pump operating for a week, must be accounted for. It may be due to the fact that the limit of the maximum internal tension is the normal internal pressure of the liquid. Exact values for the internal pressures of the alcohols are lacking but approximations are generally of the order of 3500 kg. per sq. cm. Measurements above about 1500 kg. per sq. cm. or a relative vapor pressure of 0.012 are not available from this work in the case of propyl alcohol or above about 2000 kg. per sq. cm. or a relative vapor pressure of 0.035 in the case of methyl alcohol. At these pressures the desorption volumes of water washed samples agree for all three liquids. But from the volume of propyl alcohol retained after much evacuation it seems that, for propyl alcohol, the limit is about 1700 kg. per sq. cm. If this is the sole factor in this range, either the pump could not produce a better vacuum than about 0.16 mm., or the accepted approximate internal pressure values of the alcohols are high. It is more probable that some other factor is involved.

If the structure of the cellulose is such that these voids which contain the liquid may be closed off by bonding of a comparatively narrow neck, then it is conceivable that some parts might be sealed off while still containing liquid which would not be removed by evacuation. Support is lent to this idea by some other experiments not yet ready for publication. This explanation would also account for the peculiar shape of the adsorption curve in the low vapor pressure region. If some alcohol were held in such pockets, regardless of the low vapor pressure, it would be nearly constant in amount until sufficient liquid became sorbed to open the sealed neck of the pocket, and only after this occurred would it participate in the more general phenomena.

The effect of temperature on the amount of residual alcohol or water throws no definite light on the manner in which it is held, except to indicate that vapor pressure is still active in the phenomenon. In the experiment on the effect of temperature on the amount of residual water, the amount lost on raising the temperature was regained on lowering it. This could not be the case if it were only a matter of increasing the temperature to open some pockets to allow the escape of water trapped in the pockets.

While it cannot be said that the hypothesis is proved by the experimental results, it is claimed that it accords with these results.

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXVII. METHYLATION AND STRUCTURE OF METHANOL LIGNIN (SPRUCE)[1]

BY JACK COMPTON[2] AND HAROLD HIBBERT[3]

Abstract

The composition of spruce methanol lignin prepared by the action of anhydrous methanol-hydrogen chloride on spruce meal was found to vary with the temperature and time of extraction. The reaction mixture contains two products, having methoxyl contents of 21.6 and 24%, respectively. Higher temperatures and longer time of heating favor formation of the latter. Long continued extraction of the crude methanol lignin with ether removed the second product (OCH_3, 24%). This showed that this was a true "ether-soluble" fraction, but it was not found possible to isolate the pure methanol lignin (OCH_3, 21.6%) by this process. The two substances can be separated either by solvent extraction or, as now shown, by use of 8-10% sodium hydroxide. Methylation of methanol lignin with dimethyl sulphate and alkali gives rise to the formation of new hydroxyl groups, the extent of the changes increasing markedly with rise in temperature of methylation and with increase in concentration of alkali used.

A methanol lignin (OCH_3, 22.3%) on repeated methylation yields a methylated lignin containing 37.2% methoxyl. Degradation during methylation is restricted by the use of acetone as solvent and only a slight excess of alkali (5-10%) at 20° C. The results indicate the necessity for caution in the interpretation of data based on methylation experiments involving the use of alkali, and point to the presence of heterocyclic oxygen rings, non-furane in type, as part of the lignin structure. When refluxed for 48 hr. with 65% aqueous methyl alcohol containing 9% sulphuric acid, ether-insoluble methanol lignin (OCH_3, 22.3%) yielded a product with methoxyl content 21.3% which decreased to 20.9% when the product was treated for a further 52 hr.

Introduction

In a previous communication (2) it was shown that crude methanol lignin (OCH_3, approximately 23%) prepared from spruce wood-meal by the action of anhydrous methanol-hydrogen chloride solution contains two products, an ether-dioxane soluble product corresponding to true methanol lignin (OCH_3, 21.6%) (1) and a second ether-dioxane soluble product (OCH_3, 23.6%), the ratio of the two being dependent on the temperature of extraction. Higher temperatures favored the formation of the second derivative.

Their separation can be readily effected (2) by fractionation of the crude methanol lignin first from dioxane-ether solution followed by dioxane-benzene precipitation. It is shown in the experimental part that a similar separation can be effected by the use of 8-10% sodium hydroxide solution at room temperature.

In view of these results and the importance attached to methylation studies as bearing on the structure of lignin, it seemed advisable to investigate the changes, if any, brought about by varying the temperature and quantity of alkali used in the methylation of methanol lignin with dimethyl sulphate, since this procedure is generally regarded as one of the fundamental reactions of all types of lignin. Holmberg and Wintzell (6), using this reagent, methy-

lated two fractions of alkali lignin, designated "α-" and "γ-alkali lignin" with methoxyl contents of 15.4 and 14.6% to give methylated products of 23.4 and 23.2%, respectively. Urban (9) methylated "Willstätter lignin" (OCH_3, 15.5%) with dimethyl sulphate and 45% potassium hydroxide at 80-100° C. A methoxyl content of 28.2% was obtained after 15 methylations, while at temperatures below 25° C. the product contained 32.4% methoxyl after two methylations. Heuser and Samuelsen (5), using dimethyl sulphate and 10% sodium hydroxide, methylated lignin sulphonic acid (OCH_3, 13.1%) and obtained after five methylations a product with a methoxyl content of 25.4%. Brauns and Hibbert (1) methylated methanol lignin (OCH_3, 21.6%) completely with dimethyl sulphate and 30% sodium hydroxide at 56-60° C., the fully methylated product having a methoxyl content of 32.2%. Recently Harris, Sherrard and Mitchell (3), in an investigation on the progressive methylation of Klason lignin (72% sulphuric acid) with dimethyl sulphate and sodium hydroxide, obtained a completely methylated lignin with methoxyl content of 32.2%, in agreement with the value obtained for fully methylated methanol lignin (1).

In the present investigation the methanol lignin used was the ether-dioxane insoluble material (OCH_3, 22.3%) obtained by dissolving crude methanol lignin in dioxane and precipitating with ether (2). As already indicated this product is a mixture of two substances with methoxyl contents of 21.5 and 24.5%, respectively. This crude product on methylation with dimethyl sulphate under mild conditions (20-40° C., and using only a slight excess of 7.5 N sodium hydroxide) yielded two methylated methanol lignins with methoxyl contents of 32.2% (A) and 35.4% (B), respectively. More drastic methylation (60° C. and a large excess of alkali) yielded a more highly methylated product (C) (OCH_3, 37.2%) in addition to (B). Repeated treatment of (A) and (B) with the same methylating reagents showed that: (i) The presence of a large excess of alkali and an increase in temperature brings about partial conversion of (A) into (B); (ii) A large excess of alkali causes partial conversion of (B) into (C). Evidently the lignin molecule at higher temperatures and in presence of excess alkali reacts to form new hydroxyl groups capable of methylation. The best methylating conditions for avoiding structural changes are found to be the use of:—(a) acetone as solvent; (b) a slight excess of alkali (5-10%); and (c) a temperature of 20° C., but in view of the above results it is evident that caution is necessary in drawing any conclusions regarding structure based on methylation studies.

Proof that free hydroxyl groups are formed during drastic methylation of methanol lignin resulting in the conversion of $A \rightarrow B \rightarrow C$ is shown in the fact that neither (A) nor (B) undergoes acetylation with acetic anhydride in pyridine solution. This indicates probable absence of free hydroxyl groups in these fractions. The efficiency of these reagents for the acetylation of lignin has been proved both by Pringsheim and Magnus (8) and by Heuser and Ackermann (4). The latter authors found that these reagents gave a higher acetyl content than that obtained with any other reagents.

Acetylation of ether-insoluble methanol lignin (OCH₃, 21.0%) yields an acetylated lignin (OCH₃, 17.6%), whereas the ether-soluble product (OCH₃, 24.2%) gives an acetylated product containing OCH₃, 20.2%, indicating a different ratio of hydroxyl to methoxyl in each case. Fractionation, after acetylation, of methanol lignin (OCH₃, 22.3%) yields an ether-insoluble fraction (OCH₃, 18.4%) and an ether-soluble fraction (OCH₃, 19.3%). This provides additional evidence that the methanol lignin (OCH₃, 22.3%) is a mixture.

The ease with which new hydroxyl groups are formed on methylation would appear to offer supporting evidence for the presence of heterocyclic oxygen rings of a non-furane type.

Action of Acids on Methanol Lignin

When methanol lignin with a methoxyl content of 22.3% is refluxed with 9% sulphuric acid in aqueous methanol solution (65%) for a period of 24 hr., an ether-insoluble lignin with a methoxyl content of 21.3% is obtained, which value decreases to 20.9% on refluxing for a further 28 hr.

Experimental

The crude methanol lignin was prepared by the method described previously (2), and was fractionated three times by dioxane-ether precipitation. The ether-soluble fraction was isolated by removal of the excess solvents and precipitation with petroleum ether (2). The results are given in Table I.

Long continued ether extraction of the crude methanol lignin (OCH₃, 23.0%) removed one of the products (OCH₃, 24%). This showed that the latter was a true "ether-soluble" fraction, but it was not found possible to isolate the pure methanol lignin (OCH₃, 21.6%) by this process. As shown previously (2) this can be effected by substituting dioxane-benzene for dioxane-petroleum ether as precipitating medium.

TABLE I

FRACTIONATION OF CRUDE METHANOL LIGNIN
(OCH₃, 23.0%)

(By use of dioxane-ether)

No. of fractionation	Amount used, gm.	Yield		Methoxyl content	
		Ether insol., gm.	Ether sol., gm.	Ether insol., %	Ether sol., %
1st	55	44.5	7.50	22.9	24.1
2nd	20	17.8	1.05	22.2	24.5
3rd	17.8	17.0	0.55	22.3	24.2

Fractionation of Methanol Lignin with Alkali (8-10%)

Methanol lignin (1 gm.; OCH₃, 21.7%) prepared from spruce wood-meal previously extracted with 5% sodium hydroxide in an atmosphere of nitrogen, was warmed slightly with 8-10% sodium hydroxide (50 cc.), the solution allowed to stand for two hours, and then filtered through a sintered glass funnel. The soluble lignin fraction (7) was isolated by adding the filtrate dropwise to cold 1% hydrochloric acid, filtering, washing, drying, and finally

purifying the lignin by precipitation from dioxane and ether. Yield, 0.86 gm. (86%); OCH_3, 21.5%. The insoluble lignin fraction was washed with 1% acetic acid, then with water, dried, dissolved in dioxane and reprecipitated by ether. Yield, 0.14 gm. (14%); OCH_3, 23.2%. The above fractionation by means of alkali is possible only with an alkali concentration not less than 8-10%, owing to the complete solubility of the lignin at lower concentrations.

METHYLATION OF METHANOL LIGNIN WITH DIMETHYL SULPHATE AND ALKALI

Effect of Temperature and Concentration of Alkali on Methylation of Methanol Lignin (OCH_3, 22.3%)

Experiment I. Methylation at 20° C. in acetone solution using 7.5 N sodium hydroxide in 5% excess:—The methanol lignin (2.0 gm.) was dissolved in 2% sodium hydroxide solution (15 cc.), acetone (26 cc.) was added and the solution then treated with five additions each of dimethyl sulphate (5.3 cc.) and 7.5 N sodium hydroxide (7.85 cc.) during one-hour intervals. In each separate addition the reagents were added simultaneously over a period of 15 to 30 min. with rapid stirring which was continued until the end of the hour period, when the next addition was made in the same manner. On completion of the last addition the mixture was stirred for one and one-half hours, and the acetone then removed at 20° C. under diminished pressure. The alkaline mixture, after dilution to 180 cc. with water, was filtered, the residual product ground to a fine powder, thoroughly washed with water, and dried. The crude product was dissolved in anhydrous dioxane (15-20 cc.), centrifuged, filtered and precipitated by pouring into 225 cc. of anhydrous ether. The light, buff-colored product so obtained, after washing thoroughly with anhydrous ether followed by petroleum ether (b.p. 80-90° C.), was finally washed twice with petroleum ether (b.p. 30-50° C.). Yield of ether-insoluble material (Fraction *A*), 0.95 gm.; OCH_3, 32.3%. The ether-dioxane solutions obtained were combined, concentrated and precipitated with petroleum ether. This yielded Fraction *B* (ether-soluble). Yield, 0.80 gm.; OCH_3, 35.3%. Further methylation of either fraction brought about no appreciable change in methoxyl content.

Experiments II, III, IV and V. The experimental conditions employed are indicated on the accompanying chart. The remethylations were carried out in the same specific manner for each individual experiment.

Experiment II. The results indicate formation of Fraction *B* from *A*, while remethylation of Fraction *B* yields a new product, Fraction *C* (OCH_3, 36.5%).

Experiment III. The almost complete conversion of Fraction *A* into *B* was indicated.

Experiment IV. Partial conversion of Fraction *B* into a more highly methylated product, Fraction *C*, was shown.

METHYLATION OF METHANOL LIGNIN AND ACETYLATED METHANOL LIGNIN IN ACETONE USING 7.5 N SODIUM HYDROXIDE SOLUTION

Methanol lignin, OCH₃, 22.3%

Acetylated methanol lignin, OCH₃, 18.9%

Expt. I. Methylation at 20° C. using 5% excess alkali

Ether insol. fraction (A) OCH₃, 32.3% Yield, 47.5%

Ether sol. fraction (B) OCH₃, 35.3% Yield, 40%

Remethylation — No change

Remethylation — No change

(A) Ether insoluble fraction OCH₃, 32.3%

Expt. II. Methylation at 20° C. using 50% excess alkali

Ether insol. fraction OCH₃, 32.3% Yield, 45%

Ether sol. fraction OCH₃, 35.6% Yield, 31%

Remethylation (B) OCH₃, 33.1% (mixture of products A and B)

Remethylation OCH₃, 36.5% (mixture of products B and C)

Expt. III. Methylation at 40° C. using 5% excess alkali

Ether insol. fraction OCH₃, 32.6% Yield, 40%

Ether sol. fraction OCH₃, 34.9% Yield, 42%

Remethylation OCH₃, 34.1% (mixture of products A and B) (B)

Ether sol. fraction OCH₃, 35.2%

Remethylation OCH₃, 35.3% (B)

Expt. IV. Methylation at 40° C. using 50% excess alkali

Ether insol. fraction OCH₃, 31.9% Yield, 55%

Ether sol. fraction OCH₃, 35.5% Yield, 25%

Remethylation OCH₃, 33.6% (mixture of products A and B)

Ether sol. fraction (B) OCH₃, 35.4%

Remethylation

Ether insol. fraction (none)

Ether sol. fraction OCH₃, 36.3% (mixture of products B and C)

(B) Ether soluble fraction OCH₃, 35.4%

Expt. V. Methylation at 56-60° C. using 50% excess alkali

Ether insol. fraction OCH₃, 34.5% Yield, 75%

Ether sol. fraction OCH₃, 37.2% Yield, 17%

Remethylation — No change

Remethylation OCH₃, 34.5% (mixture of products A and B) Yield, 84%

Ether sol. fraction (C) OCH₃, 36.5% Yield, 12%

Fractionation by dioxane-ether

Ether insol. fraction OCH₃, 33.4% (mixture of products A and B) Yield, 51%

Ether sol. fraction (B) OCH₃, 35.6% Yield, 46%

(C) Ether petroleum-ether soluble fraction OCH₃, 37%

Experiment V. In this experiment, in order to obtain a *maximum* methoxyl value the starting material used was a fully acetylated methanol lignin (OCH_3, 18.9%). Fraction *A* was partially converted into Fraction *C* with a methoxyl value of 37.2%—the highest yet reported for a methylated lignin.

Experiment VI. Methylation of the ether-soluble fraction of methanol lignin (OCH_3, 24.5%, Table I). The material (1 gm.) was methylated at 20° C. using 5% excess 7.5 N sodium hydroxide solution. The methylated product was purified as described above, except that petroleum ether (b.p. 30-50° C.) was substituted for ether as precipitating agent owing to the ready solubility of the methylated product in the latter. Yield, 0.9 gm.; OCH_3, 32.6%. Remethylation gave 0.8 gm. of a more highly methylated product (OCH_3, 34.8%).

It follows that the ether-soluble methanol lignin (OCH_3, 24.5%) can be methylated directly to the ether-soluble methylated product (OCH_3, 35%), since it has been shown (Expt. I) that under these mild conditions the ether-insoluble product (OCH_3, 32%) is not converted into ether-soluble material.

Acetylation of Methanol Lignins

Acetylation experiments provide further evidence that methanol lignin (OCH_3, 22.3%) is composed of two methanol lignins (OCH_3, 21 and 24% respectively), but the separation is not as clearly defined as in the case of the pure methanol lignins (Expts. I and II).

Experiment VII. Acetylation of methanol lignin (OCH_3, 22.3%, Table I). Methanol lignin (5 gm.) was acetylated in the usual manner with pyridine and acetic anhydride and purified from dioxane-ether. Yield of ether-insoluble product, 2.8 gm.; OCH_3, 18.4%. The ether-dioxane solution, after being concentrated to a small volume, was poured, with vigorous stirring, into low-boiling petroleum ether. The precipitated product was thoroughly washed with petroleum ether and dried. Yield of ether-soluble product, 2.5 gm.; OCH_3, 19.3%.

Experiment VIII. Acetylation of the ether-insoluble fraction of methanol lignin (OCH_3, 21.3%). Ether-insoluble methanol lignin (1.0 gm.) was acetylated similarly and the reaction product isolated as above. Yield of ether-insoluble acetylated lignin, 0.9 gm.; OCH_3, 17.4%. Yield of ether-soluble acetylated lignin, 0.2 gm.; OCH_3, 17.9%.

Experiment IX. Acetylation of the ether-soluble fraction of methanol lignin (OCH_3, 24.2%, Table I). Ether-soluble methanol lignin (0.5 gm.) was acetylated as described above. After 48 hr. the acetylated product was precipitated and purified. It was found to be completely soluble in ether. It was therefore necessary to use low-boiling petroleum ether for precipitation. Yield, 0.48 gm.; OCH_3, 20.2%.

It may readily be seen that the methoxyl content of the ether-insoluble portion (Expt. VII) agrees approximately with that of the acetylated lignin obtained in Expt. VIII, whereas the methoxyl content of the ether-soluble portion of the former approaches that of the acetylated lignin obtained in this experiment (IX).

Attempted Acetylation of the Ether-insoluble and Ether-soluble Fully Methylated Methanol Lignins

Experiment X. Ether-insoluble methylated lignin (OCH₃, 32.3%). Fully methylated ether-insoluble methanol lignin (0.5 gm.) was acetylated as above. The finely divided, buff-colored powder was purified by addition of the dioxane solution to petroleum ether. Yield, 0.4 gm.; OCH₃, 32.4%.

Experiment XI. Ether-soluble methylated lignin (OCH₃, 35.3%). Fully methylated ether-soluble methanol lignin (0.5 gm.) was acetylated and purified. Yield, 0.45 gm.; OCH₃, 35.4%.

In neither Expt. X nor XI was any decrease found in the methoxyl content after acetylation. This indicated the probable absence of free hydroxyl groups.

Experiment XII. Action of 9% sulphuric acid solution on methanol lignin. Methanol lignin (OCH₃, 22.3%, 2 gm.) was dissolved in warm absolute methanol (130 cc.) and an aqueous 25% sulphuric acid solution (70 cc.) slowly added, during 10 min., in order to avoid precipitation of the lignin. After refluxing for 24 hr., one-half of the solution was removed, filtered hot and the filtrate diluted with cold water (1000 cc.). The lignin was centrifuged, washed with water, then with saturated sodium bicarbonate solution, finally twice with distilled water, again centrifuged and dried in a vacuum desiccator over calcium chloride. It was then dissolved in dioxane solution (25 cc.), centrifuged, filtered, and the lignin precipitated by pouring the solution in a fine stream into dry ether (250 cc.), with vigorous stirring. After washing with ether and then three times with petroleum ether, the product was dried over sulphuric acid. Yield, 0.9 gm.; OCH₃, 21.3%.

The remaining half of the original solution was refluxed for a further 28 hr. and the lignin isolated as above. Yield, 0.9 gm.; OCH₃, 20.9%.

In both cases the ether-soluble portion was negligible, being less than 0.1 gm.

In a further similar experiment in which 1 gm. of lignin was used, the time of hydrolysis was extended to seven days. The small amount of insoluble product was removed by filtering the hot solution and treating the filtrate as described above. Yield, 0.7 gm.; OCH₃, 21.1%.

The lignin portion which separated from the hydrolysis mixture (0.3 gm.) was ground to a fine powder, washed thoroughly with water and dried. It was only slightly soluble in dioxane, but on analysis both dioxane-insoluble and soluble fractions were found to have the same methoxyl value. Dioxane-soluble lignin fraction: OCH₃, 17.9%; dioxane-insoluble lignin fraction: OCH₃, 17.9%.

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DERIVATIVES OF SUBSTITUTED SUCCINIC ACIDS

II. THE CONVERSION OF αα'-DIARYLSUCCINAMIDES INTO DIARYLACETIC ACIDS[1]

By John A. McRae,[2] William R. Conn[3] and Kenneth J. Platt[4]

Abstract

p-Methyl-, *p*-chloro- and *p*-bromodiphenylsuccinamides have been prepared, and their behavior toward alkaline sodium hypobromite under the conditions of the Hofmann reaction has been investigated. The three amides yield as principal products *p*-methyl-, *p*-chloro- and *p*-bromo-diphenylacetic acids. It may be concluded that this behavior is characteristic of αα'-diarylsuccinamides.

Introduction

It has been shown recently (8) that αα'-diphenylsuccinamide is converted into diphenylacetic acid by alkaline sodium hypobromite under the conditions of the Hofmann reaction. To ascertain to what degree this may be considered a general reaction of αα'-diaryl succinamides, three other amides of the same type, namely α-phenyl-α'-*p*-tolysuccinamide, α-phenyl-α'-*p*-chlorophenyl-succinamide and α-phenyl-α'-*p*-bromophenylsuccinamide were prepared and their behavior toward alkaline sodium hypobromite was studied. In each case proof was obtained that when these amides are treated first in the cold with alkaline sodium hypobromite and then warmed to 80° C., after the concentration of alkali has been considerably increased, a diarylacetic acid is the principal product of the reaction, although the reaction is always accompanied by evolution of ammonia and benzaldehyde.

Purification of the diarylacetic acids thus formed, to the degree requisite for identification, was rendered difficult by the presence of small amounts of other substances that were retained obstinately. For identification recourse was made to the anilides which, in the first two instances, were compared with authentic specimens of the anilides in question.

These diarylsuccinamides were prepared severally by hydrolysis of the corresponding dinitriles by the methods of Lapworth and McRae (7) for the preparation of diphenylsuccinonitrile and -amide. α-Phenyl-α'-*p*-tolylsuccinonitrile and α-phenyl-α'-*p*-chlorophenylsuccinonitrile were prepared by the addition of hydrogen cyanide to the unsaturated nitriles produced by condensing *p*-toluic aldehyde and *p*-chlorobenzaldehyde respectively with phenylacetonitrile. The bromo-compound was prepared by a similar addition of hydrogen cyanide to α-(*p*-bromophenyl)-cinnamonitrile made from benzaldehyde and *p*-bromophenylacetonitrile.

The anilides of phenyl-*p*-tolylacetic acid and of *p*-chlorodiphenylacetic acid made for comparison were obtained in the usual way from these acids. These

acids were made according to Gyr's method (5) by the condensation of either the appropriate mandelic acid with benzene or mandelic acid with the appropriate benzene derivative by means of fuming stannic chloride. *p*-Bromodiphenylacetic acid was not obtained in sufficient quantity for use when *p*-bromomandelic acid was used. The required mandelic acids were prepared most readily by Collet's method (3).

Further experiments are in progress to elucidate the nature of the changes involved in these rearrangements, and also to study the effect of substituents of a different character.

Experimental

α-Phenyl-p-methylcinnamonitrile. This nitrile was prepared from *p*-tolualdehyde and phenylacetonitrile according to the method of Bistrzycki and Stelling (1), and was obtained always as an oil even when both the aldehyde and nitrile were distilled freshly under reduced pressure. The oil did not solidify on standing. It was therefore distilled under reduced pressure, b.p. 254° C./44 mm. The distillates from some preparations solidified quickly in part, others remained fluid for months without any separation of the solid phase. The separated solid on recrystallization had the melting point of 61° C.* given for the substance by Bistrzycki and Stelling. The oily portion reacted with hydrogen cyanide as readily as the recrystallized solid fraction. The oil may be a stereoisomeride. If this is the case it would be expected that the two isomerides would yield isomeric *α*-phenyl-*α'*-*p*-tolylsuccinonitriles on addition with hydrogen cyanide. This was not observed.

α-Phenyl-α'-p-tolylsuccinodinitrile. This nitrile was prepared as follows. The above-mentioned unsaturated nitrile (40.2 gm.) was dissolved in 800 cc. of hot alcohol. To this boiling solution 28 gm. of potassium cyanide was added in the course of 15 min. This was followed by the gradual addition (15 min.) of 24 gm. of ammonium chloride according to the modification of Brand and Loehr (2). Toward the end of the latter addition the dinitrile began to separate. The mixture was heated under the reflux for an hour. The dinitrile which separated after cooling was collected, washed with alcohol, and hot water. Yield, 39.5 gm., or 88% of the calculated amount. Recrystallized from hot alcohol the substance melted at 195° C. Calcd. for $C_{17}H_{14}N_2$: N, 11.38%. Found: N, 11.65%.

α-Phenyl-α'-p-tolylsuccinic diamide. This was prepared by hydrolyzing the dinitrile by warming 47 gm. of it with 930 cc. of 85% sulphuric acid on the steam bath until solution was effected. On pouring the solution into water the diamide separated. It was digested with cold 3% sodium hydroxide. An almost quantitative yield of crude amide was obtained. For analysis it was recrystallized several times from hot acetic acid in which it is moderately soluble; m.p. 294° C. (corr.) with decomposition. Calcd. for $C_{17}H_{18}O_2N_2$: N, 9.93%. Found: N, 10.3%.

*Unless otherwise stated, melting points are uncorrected.

α-Phenyl-α'-p-tolylsuccinic acid. $C_6H_5.CH(CO_2H).CH(C_7H_7)CO_2H$. This acid was obtained in small amounts by acidifying the caustic soda washings of the diamide. It is best recrystallized from alcohol from which it was obtained in colorless platelets, m.p. 224° C. Calcd. for $C_{17}H_{16}O_4$: C, 71.83; H, 5.63%. Found: C, 71.80; H, 5.92%. $C_{17}H_{16}O_4$ requires an equivalent 142. Equivalent found: 141.

Diethyl α-phenyl-α'-p-tolylsuccinate. This ester was obtained from the acid in the usual way. On recrystallization it separated from alcohol in thick needles, m.p. 97° C. Calcd. for $C_{21}H_{24}O_4$: C, 74.12; H, 7.06%. Found: C, 73.9; H, 7.2%.

Action of Sodium Hypobromite on α-Phenyl-α'-p-tolylsuccinamide

The sodium hypobromite solution used was made as previously described (8) from 32 gm. of bromine, 40 gm. of sodium hydroxide and 200 cc. of water. To this solution, maintained at $-10°$ C. and efficiently stirred, the recrystallized phenyltolylsuccinamide made into a thin paste with water was added during a period of 15 min. The stirring was continued for 30 min., after which the temperature was allowed to rise to 0° C. At this point 24 gm. of sodium hydroxide was added and the mixture heated to 75–80° C. on the water bath. During this heating, ammonia and either benzaldehyde or tolualdehyde or both were released, and at the conclusion of the heating a residue of 4 gm. remained undissolved. Recrystallization showed that this was the unchanged amide. Ether extracted only traces of material. Acidification with hydrochloric acid produced a heavy gummy precipitate. After several methods of purification had been tried the difficultly soluble calcium salt of the acid was obtained by addition of calcium chloride to the solution of the precipitate in ammonia. Gyr (5) had used the calcium salt in purifying his phenyltolylacetic acid. On collecting the calcium salt and reprecipitating the acid, only a slight improvement in quality was shown. The acidic substance was therefore converted into an anilide by rubbing 13 gm. of it with 49 gm. of phosphorus pentachloride, dissolving the crude acid chloride in ligroin and mixing the ligroin extract with 6 gm. of aniline. The anilide which separated was freed from unchanged aniline and recrystallized from dilute alcohol, m.p. 154–155° C. It did not lower the melting point of a sample of genuine phenyl-p-tolylacetanilide. Calcd. for $C_{21}H_{19}ON$: N, 4.65%. Found: N, 4.89%.

Phenyl-p-tolylacetanilide. $C_6H_5(C_7H_7.)CH.CONH C_6H_5$

The requisite phenyl-p-tolylacetic acid was made according to the directions of Gyr by condensing mandelic acid and toluene by means of fuming stannic chloride. Difficulty was experienced in purifying the acid thoroughly. It was converted into the anilide, and the anilide, recrystallized from hot alcohol, was obtained as fine needles; m.p. 154°–155° C. Calcd. for $C_{21}H_{19}ON$: C, 83.72; H, 6.30%. Found: C, 83.83; H, 6.04%.

α-Phenyl-α'-p-chlorophenylsuccinodinitrile. $ClC_6H_4 . CH(CN) . CH(C_6H_5)CN$

α-Phenyl-*p*-chlorocinnamonitrile was prepared from *p*-chlorobenzaldehyde and phenylacetonitrile according to von Walther and Raetze (9). The method used for the addition of hydrogen cyanide was almost identical with that used for the *p*-methyl derivative. The solutions and proportions used were 20 gm. of this nitrile in 700 cc. of hot alcohol, 14 gm. of potassium cyanide in 40 cc. of water and 12 gm. of ammonium chloride in 40 cc. of water. After heating on the steam bath for three hours under the reflux, 18.5 gm. of the addition compound separated. After several recrystallizations from alcohol the substance melted consistently at 225° C. Calcd. for $C_{16}H_{11}N_2Cl$: N, 10.51; Cl, 13.32%. Found: N, 10.75; Cl, 13.06%.

α-Phenyl-α'-p-chlorophenylsuccinic Diamide. $ClC_6H_4(CONH_2) . CH(C_6H_5)$
   $CONH_2$

The above-mentioned nitrile (8 gm.) was hydrolyzed to the diamide by dissolving it in 50 cc. of 90% sulphuric acid on the steam bath and then pouring the solution into water. The amide that separated was washed with caustic soda and recrystallized from glacial acetic acid, m.p. 296° C. (corr.). Calcd. for $C_{16}H_{15}O_2N_2Cl$: N, 9.26; Cl, 11.74%. Found: N, 9.53; Cl, 11.64%.

α-Phenyl-α'-p-chlorophenylsuccinic Acid

This was prepared by dissolving the amide (10 gm.) in 50 cc. of 90% sulphuric acid at 100° C., diluting with boiling water until the substance just remained in solution and then heating for four hours at 125° C. under a reflux. The acid obtained by further dilution was recrystallized from alcohol, m.p. 240–241° C. Calcd. for $C_{16}H_{13}O_4Cl$: Cl, 11.75%. Found: Cl, 11.55%.

The Action of Sodium Hypobromite on p-Chlorodiphenylsuccinamide

The conditions used were identical with those already described for phenyl-tolylsuccinamide. As before, ammonia and benzaldehyde were evolved during the heating and from 6.7 gm. amide a residue of 1.3 gm. remained undissolved. Acidification produced a gummy precipitate which could be partially purified by recrystallization from hot water. This material was converted into the anilide which on repeated crystallizations from hot alcohol was obtained in long needles melting at 179° C. The substance did not depress the melting point of *p*-chlorodiphenylacetanilide. The identity of this substance with the latter was confirmed further by analysis. Calcd. for $C_{20}H_{16}ONCl$: N, 4.36; Cl, 11.04%. Found: N, 4.62; Cl, 10.75%.

p-Chlorodiphenylacetanilide

p-Chloromandelic acid was prepared by Collet's method (3) by converting *p*-chloroacetophenone into the ω-ω-dibromoderivative and treating this with 5% potassium hydroxide. The acid was obtained in 39% yield calculated on the dibromo-compound used, and its description agreed with that given by Collet. A mixture of *p*-chloromandelic acid (18 gm.) in 90 cc. of boiling

benzene with 40 gm. of fuming stannic chloride was refluxed for six hours; dilution and extraction with ether gave 18 gm. crude *p*-chlorodiphenylacetic acid. The anilide was made from this acid and recrystallized from alcohol, m.p. 179° C. Calcd. for $C_{20}H_{16}ONCl$: N, 4.36%. Found: N, 4.51%.

α-*Phenyl-α'-p-bromophenylsuccinodinitrile*

Instead of combining *p*-bromobenzaldehyde with phenylacetonitrile, it was found more feasible to combine benzaldehyde with *p*-bromobenzyl cyanide and add hydrogen cyanide to the resulting nitrile. The necessary *p*-bromophenylacetonitrile was obtained in excellent yield by the action of potassium cyanide on *p*-bromobenzyl chloride instead of the bromide used by Jackson and Lowery (6). It condensed readily with benzaldehyde as described by Frost (4).

The addition of hydrogen cyanide to the α-bromophenyl-cinnamonitrile took place in almost quantitative yield, when to the nitrile (10 gm.) dissolved in 400 cc. of hot alcohol was added a solution of 7 gm. of potassium cyanide in 20 cc. of water, followed by the gradual addition of 6 gm. of ammonium chloride in 20 cc. of water, and the whole heated for 30 min. The *p*-bromo-diphenylsuccinodinitrile which separated was recrystallized from glacial acetic acid, m.p. 213–214° C. (corr.). Calcd. for $C_6H_{11}N_2Br$: N, 9.00; Br, 25.72%. Found: N, 8.94; Br, 24.9%.

α-*Phenyl-α'-p-bromophenylsuccinic Diamide*

The above-mentioned dinitrile was dissolved in warm 90% sulphuric acid and after a short time the solution was cooled and diluted. The amide separated and after washing it with dilute caustic soda it was recrystallized from glacial acetic acid in which it is moderately soluble when hot, m.p. 300–301°C. (corr.) with decomposition. Calcd. for $C_{16}H_{15}O_2N_2Br$: N, 8.07; Br, 23.1%. Found: N, 8.1; Br, 23.5%.

The Action of Sodium Hypobromite on p-Bromo-diphenylsuccinamide

Exactly the same conditions were employed as with phenyltolylsuccin-amide; 25.9 gm. of *p*-bromodiphenylsuccinamide was used. A considerable amount of amide seemed to remain undissolved in the cold solution, but on heating for three hours at 75–80° C., as previously described, all but 4.2 gm. dissolved. This on recrystallization was identified as unchanged amide and was confirmed by analysis. Found: N, 8.1; Br, 23.4%. The filtrate on standing for some time deposited further crystalline matter but in quantity too small for identification. Recrystallized from acetic acid it melted at 233° C. After removal of this crystalline deposit the filtrate was acidified and a gummy precipitate was thrown down. Various attempts to purify it thoroughly failed. It was therefore converted into the anilide. This was crystallized repeatedly from alcohol and it melted at 177–178° C. The analytical figures agree with those required for *p*-bromodiphenylacetanilide. Calcd. for $C_{20}H_{16}ONBr$: C, 65.6; H, 4.37; N, 3.83; Br. 21.9% Found: C, 65.7; H, 4.64; N, 3.99; Br. 21.8%.

An attempt was made to obtain *p*-bromodiphenyl acetanilide for comparison. *p*-Bromomandelic acid was made from *p*-bromoacetophenone according to the directions of Collet, but the authors were unsuccessful in their efforts to isolate bromodiphenylacetic acid from the product of the action of fuming stannic chloride on this mandelic acid dissolved in boiling benzene.

Acknowledgment

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THE EFFECT OF REGAIN ON THE RATE OF ADSORPTION OF STANNIC CHLORIDE BY SILK FIBROIN[1]

BY G. V. JANSEN[2] AND E. A. SMITH[3]

Abstract

The effect of the moisture content of silk fibroin on the amount of weighting it takes up in given periods of time from a 30° Bé. stannic chloride solution has been determined. Saturated silk (>35% moisture content) attains maximum adsorption much faster than does dry silk, whereas a minimum rate of adsorption exists for silk of about 10–23% moisture content. An explanation has been advanced for these phenomena based on the rate of swelling of silk in water and in stannic chloride solution, the size of the pores in dry silk and the effect that the water in these pores would have on the stannic chloride solution entering them. It is pointed out that the weighting taken up by silk from stannic chloride solutions is probably adsorbed not as stannic chloride but as a mixture of the various tin complexes which have been shown to exist in aqueous stannic chloride solutions. The effect on the weighting of increasing the temperature of the hydrolyzing bath and of the addition of inorganic chlorides and sulphates to this bath has also been investigated. The final weighting retained by the silk has been shown to consist of hydrated stannic oxide, the amount of water present depending upon the conditions obtaining during hydrolysis and drying.

Introduction

The loading of silk with tin—the process consisting of soaking the silk in stannic chloride solution, followed by a hydrolysis with water and treatment with disodium phosphate—is a practice of considerable importance in the silk finishing industry, where the process is known as "weighting". The treatment can be repeated until the desired weighting is attained. Coughlin (5) has shown that the process consists of an apolar adsorption of stannic chloride molecules by the silk, and Chinn and Phelps (4) have demonstrated that it is a negative adsorption in the region of concentrations of stannic chloride most commonly used in the industry.

The work described here deals with the first phase of commercial weighting, viz., the adsorption of stannic chloride* by the silk and its hydrolysis, in the fibre, to hydrated stannic oxide, and specifically with the effect which the moisture content or "regain" of the silk has on its rate of adsorption of the stannic chloride.

* The probability that other tin complexes, rather than stannic chloride, are adsorbed, is pointed out in the body of the paper. However, for the sake of convenience, the term stannic chloride will be used when adsorption by silk from stannic chloride solutions is discussed, but it will be understood to refer to whatever tin complexes the silk actually does adsorb.

The sericin or "silk gum" was removed from the silk by treatment with hot soap solution. The silk fibroin, which is unaffected by this process, was thus obtained in a pure state. Samples of this "degummed" silk of known dry weight were then brought to the desired moisture content, at a thermostatically controlled temperature, in a suitable humidifying chamber. This process is known to the trade as "conditioning". The samples were then reweighed and immersed in a stannic chloride solution of 30° Bé. (362 gm. per litre) for various periods of time, hydrolyzed in distilled water, dried and weighed again.

Then

$$\frac{\text{(conditioned weight} - \text{original dry weight)} \times 100}{\text{original dry weight}} = \text{percentage regain,}$$

and

$$\frac{\text{(final dry weight} - \text{original dry weight)} \times 100}{\text{original dry weight}} = \text{percentage weighting.}$$

Experimental

Preparation of Samples

The silk used was a loosely woven flat crêpe of Japanese origin. It was carefully degummed at 98–100° C. in two successive soap baths containing 1 and 0.5% of soap respectively, and after several hot water rinses it was freed from the last traces of soap by extraction with 70% alcohol. The residual alcohol was removed with boiling distilled water. The silk was then adjusted to a pH of about 4, (the most acceptable value for its isoelectric point (6)), by allowing it to reach equilibrium with a solution of hydrochloric acid maintained at this pH by the necessary additions of dilute hydrochloric acid.

After the silk was air-dried, it was cut into 0.8–1.0 gm. samples which were individually dried and weighed. These were then conditioned for two months in desiccators containing saturated salt solutions of known vapor pressure, the desiccators being stored in an air thermostat at 20° C. ± 0.1°. After the samples were weighed to determine their regains, they were ready for weighting. The solutions used for conditioning are listed in Table I, together with the approximate relative humidity produced (10, p. 67; 20, p. 1273; 25, p. 328) and the regain attained by the samples in each case.

TABLE I

Solution	Approx. rel. hum. produced, %	Regain attained, % of wt. of dry silk
$KC_2H_3O_2$	20	4.1
$Na_2Cr_2O_7 . 2H_2O$	52	8.0
K_2CrO_4	88	14.1
$NH_4H_2PO_4$	93	17.0
K_2SO_4	96	19.1
H_2SO_4 (d, 1.05)	97	21.7
H_2SO_4 (d, 1.045)	97.5	22.5
H_2SO_4 (d, 1.025)	99	25.7

Weighting and Hydrolysis

A freshly prepared c.p. stannic chloride solution of 30° Bé. was used for the weighting solution, as this is the strength generally employed in the industry. The weighting was done in a one litre beaker, the stannic chloride

solution being stirred gently by means of an automatic stirrer, and maintained at 20° C. ± 1° in a water bath. The samples were plunged into this solution on removal from the weighing bottles. After the required period of immersion they were transferred to a large volume of distilled water maintained at 20° C. where the stannic chloride which they had adsorbed was hydrolyzed, and thus fixed on the fibre as a hydrated stannic oxide $SnO_2 . xH_2O$ (17, pp. 407-410; 24, p. 187) as will be discussed below. After 20 to 30 min. in the distilled water the samples were rinsed under running tap water, dried and weighed. The main series of weightings (Fig. 2) were all completed within one week, too short a period for the stannic chloride to change its state of hydrolysis appreciably during the course of the experiments (7; 13, p. 273). That the age of a stannic chloride solution does affect its rate of adsorption by silk is shown below.

Weightings were also performed with bone-dry and wringing-wet samples. The latter were soaked in distilled water overnight and then wrung out well before immersion in the stannic chloride bath. The amount of water that the silk will adsorb under these conditions should correspond to that which it will take up from a saturated atmosphere, *viz.*, 35% at 20° C. (3). The amount adsorbed will probably be slightly greater than this, as Katz (12) indicated. However, the actual equilibrium moisture content is of no great importance for the purposes of this paper, since excess water always adhered to the samples after they were wrung out. Hence the results for the wet samples were plotted on the graphs as corresponding to a regain of 35%.

Results

Fig. 1 shows the results obtained when this investigation was started (11). A weighting period of one hour was used. It was thought, at first, that the graph represented equilibrium conditions, with a distinct minimum weighting of 5% occurring for silk of 19% regain, since dry silk requires only 10–15 min. to attain maximum adsorption of stannic chloride, as Coughlin (5) has shown. However, samples of 19.1% moisture content were weighted for two hours, and they took up an average of 9.3% weighting, so that it became obvious
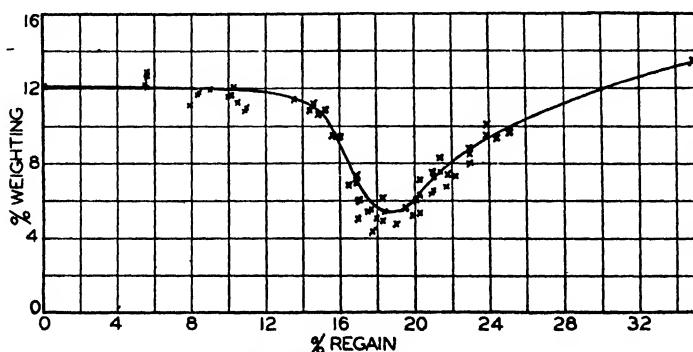
FIG. 1. *Graph showing relation between moisture content of silk and weighting taken up during a one hour immersion in 30° Bé. stannic chloride solution.*

that the regain of the silk affected the rate of its adsorption of stannic chloride, and did not affect the actual amount of adsorption at equilibrium. Accordingly, a more elaborate series of experiments were carried out when this work was resumed in 1934–35, the results of which are shown in Fig. 2. Here
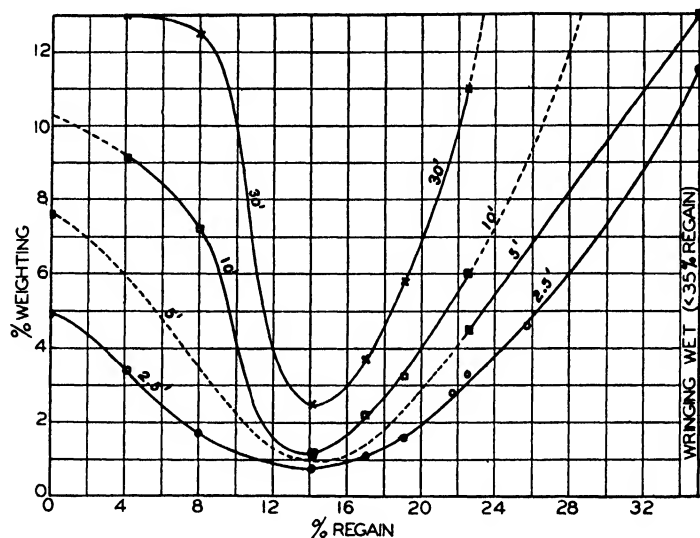
FIG. 2. *Graph showing effect of regain on weighting taken up by silk during various periods of immersion in 30° Bé. stannic chloride solution.*

TABLE II
RELATIVE WEIGHTINGS

Low weighting 2.5 min.	Medium weighting 10 min.	High weighting 30 min.
%	%	%
1.91	6.82	12.8
1.55	7.44	12.6
1.62	7.38	12.4
1.69	6.97	12.1
Av. 1.7	Av. 7.2	Av. 12.5

each point gives the average of four determinations. Points representing equal periods of immersion of the samples in the stannic chloride bath were joined by continuous lines. The usual variation in the results obtained for four separate samples is given in Table II. The figures are for the experiment in which the regain was 8%.

The maximum weighting obtained under the conditions described above was 13.1% ± 0.3.

Discussion of Results

It is apparent that there is a great variation in the rates of adsorption of stannic chloride by silk samples of different moisture content. It is rather surprising that samples saturated with water adsorb stannic chloride much faster than dry samples, and still more difficult of explanation is the fact that samples approximately half saturated with water adsorb the least amount of stannic chloride in a given period of time. The exact position of the minimum amount of adsorption on the regain base seems to vary slightly. It depends on the nature and history of the silk and also on the time during

which the silk remains immersed in the stannic chloride solution. This is clearly shown in Fig. 3, where the results obtained by Press (18) with Chinese silk are graphically represented. It is seen that samples of 13, 17.5 and 23.8% regain all attained equilibrium in about the same time, *viz.*, 110 min., but
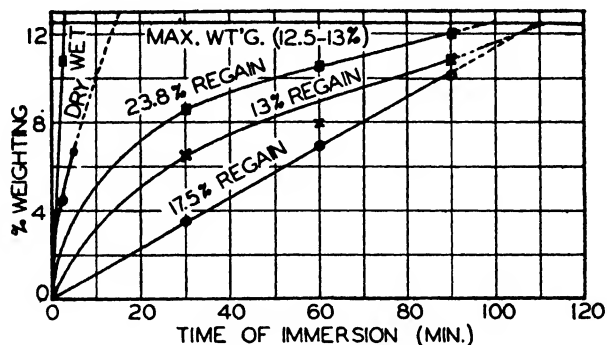
FIG. 3. *Graph showing variation in weighting with time, for silk of various moisture contents immersed in 30° Bé stannic chloride solution.*

that the weighting after 30 min. immersion was much less for the samples of 17.5% regain than for the other two sets. However, two facts stand out clearly, *viz.*, (1) saturated silk adsorbs stannic chloride much faster than does dry silk, and (2) silk of about 10–23% moisture content adsorbs stannic chloride much more slowly than even dry silk does. These phenomena are discussed below.

Discussion of Results for Dry and Saturated Silk

Since silk in a saturated and (consequently) swollen condition attained maximum adsorption of stannic chloride in less than five minutes, it is obvious that the rate of diffusion of the stannic chloride molecules into the porous network of the fibre is very rapid when the pores are enlarged, as they are in a saturated fibre. (For a complete discussion on fibre structure, swelling during water sorption, etc. see (2, 1, 15, 16, 22).) It will be sufficient to state here that the pores or intermicellar spaces in a fibre increase in size as the fibre swells during water sorption, and not the micelles themselves. Hence stannic chloride molecules must enter these pores and be adsorbed on the pore walls. On hydrolysis the resulting coagulated precipitate of $SnO_2 . xH_2O$ is left mechanically trapped in the intermicellar spaces, and the active groups in the silk are free to adsorb fresh stannic chloride molecules. Herzog and Conell (9) have shown that the X-ray photograph of the fibre of silk is not changed by weightings as high as 50 to 65%.

It seems probable that the factor which determines the time required for dry silk to attain maximum adsorption of stannic chloride is the rate of swelling of the silk in the stannic chloride solution, whereby its porous structure is made accessible to the stannic chloride molecules. To test this hypothesis, experiments were performed on the rate of swelling of silk gut in water and stannic chloride solution and on the rate of adsorption of stannic chloride by

dry and saturated gut. Silk gut (as prepared for surgical sutures) was used in preference to individual silk fibres because it could be handled much more conveniently. The silk gut is prepared by dissecting out the silk sac of the silk worm and extending the sac (15). The gut consequently consists of pure silk fibroin free from sericin. The experimental technique and results are given below.

It is of interest at this point to compare the average diameter of the pores in dry silk with that of the stannic chloride molecule. It has been found in this laboratory, that methyl and ethyl alcohols will swell dry silk gut, but that propyl or butyl alcohol will not*. It appears reasonably safe, therefore, to conclude that the pores in dry silk are too small to admit propyl alcohol and that their diameter is somewhat less than 6 Å. (Speakman (22) has found that the pores in dry wool admit the propyl alcohol molecule, and he places their diameter at 6 Å.)

The diameter of the stannic chloride molecule, calculated from its parachor as given by Sugden (23, p. 187), is about 6.5 Å. If it is assumed that the structure of silk fibre is the same as that of silk fibroin in gut form, it seems fairly certain that silk must swell to a certain extent before the pores are large enough to admit stannic chloride molecules. The same conclusion would apply to other tin complexes such as $SnCl_3OH$, H_2SnCl_6, etc. (see below), since these will in general have a molecular diameter as great as, if not greater than, that of the stannic chloride molecule.

Experiments with Silk Gut

Silk gut of diameter about 0.4 mm. was employed in the following experiments. It was washed in benzene and then in boiling water to remove surface grease and impurities before use. Samples weighing about 0.2 gm. were then weighted, at a temperature of 25° C., both in a bone-dry and in a water-saturated condition as described. Hydrolysis was allowed to proceed for 24 hr. to ensure completion. The results are shown in Table III.

TABLE III

RESULTS OF WEIGHTING SILK GUT

Period of of immersion in stannic chloride, hr.	Dry samples, % weighting	Wet samples, % weighting
0.5	0	–
6	2.2	7.9, 9.4
9.5	3.6, 3.5	–
15	4.8, 5.2	–
19.5	5.2	9.5, 12.7
48	11.3, 11.7	–
67	12.4	–

Although the results are somewhat irregular it is obvious that silk gut behaves in a manner analogous to the behavior of silk fibre in crêpe form, in that saturated samples adsorb stannic chloride much faster than do dry samples. The swelling of silk gut in stannic chloride (30° Bé.) and in distilled water at 25° C. was next determined. Photographs of

* *Details of this work will be included in a paper that the writers hope to publish in the near future.*

four samples of gut held vertically by wire supports in a small rectangular plane glass cell were taken, and the diameters of the fibre images on the photographic plates were measured with a traveling microscope. The camera produced a magnification of about two diameters. The true fibre diameter could be obtained by means of the image of a platinum wire of known diameter placed alongside the fibres in the cell. The fibres could be rotated, each about its own vertical axis. Since the gut samples were all slightly elliptical in cross section, two photographs were always taken for each determination of diameter, the fibres being rotated through an angle of 90° for the second exposure. The geometrical mean of the two figures obtained for the average diameter of any one fibre from the two plates was then taken as the mean fibre diameter. The average diameter was the arithmetical average of 10 measurements made at equally spaced intervals along the fibre length. Photographs were first taken of the dry fibres (in air) and then at various intervals of time after the swelling liquids had been poured into the cells. The results are given in Table IV.

TABLE IV

SWELLING OF SILK GUT

Time in liquid, hr.	Average lateral increase in diameter of gut samples	
	Water, %	Stannic chloride, %
6	20	11
24	21 ± 2	14
72	—	22 ± 2

These figures are slightly higher than those obtained by Lloyd and Marriott (15) (16 to 18%) for the equilibrium lateral swelling of silk gut in water and in 1 N hydrochloric acid. However, the figures represent the relative rates of swelling sufficiently accurately for our purpose, and they clearly show that silk gut swells much more rapidly in water than in stannic chloride solution, although at equilibrium the percentage of swelling is about the same in both liquids.

Furthermore, saturated silk gut attains maximum adsorption of stannic chloride in 24 hr. or less, whereas dry gut swells only to $\dfrac{14 \times 100}{22} = 64\%$ of its final value in this time. The assumption made that the rate of swelling of dry silk in the stannic chloride solution governs its rate of adsorption of stannic chloride is thus proved to be correct.

Discussion of the Minimum Rate of Adsorption

There is still left to be explained the minimum rate of adsorption of stannic chloride observed for silk which is only about half saturated with moisture (10 to 23% regain). The chief reason that dry silk swells more slowly in stannic chloride solution than in water must be due to the blocking effect that the molecules of stannic chloride produce in the intermicellar channels as they are adsorbed on the surfaces of the micelles. (The decrease in the concentration of water molecules in stannic chloride solution of 30° Bé. (1.39 moles per litre) is only about 16%). Thus the diffusion of succeeding water (and stannic chloride) molecules into the pores is hindered and the silk swells much more slowly.

Following this line of reasoning it is apparent that the pores in silk of 10 to 23% moisture content must be more immediately and more effectively blocked by adsorbed stannic chloride molecules than is the case with dry silk. That is to say, the water in the pores catalyses the adsorption of stannic chloride in some way, so that the stannic chloride molecules that first enter the pore openings are immediately adsorbed and thus greatly hinder the inward diffusion of succeeding water or stannic chloride molecules. The result is that the silk swells much more slowly, and consequently requires a much longer time to attain maximum weighting. Obviously, as the moisture content of the silk is increased beyond this critical point, the pores become larger and are not so readily blocked, so that the rate of adsorption of stannic chloride increases with the moisture content and reaches a maximum for completely saturated silk.

The only apparent effect that the water in the silk pores could have on the stannic chloride would be to increase its degree of hydrolysis. The hydrolysis occurring in aqueous stannic chloride solutions is discussed below. The experiments described in the following paragraph were devised to ascertain whether stannic chloride is actually adsorbed more rapidly by silk when its degree of hydrolysis is increased.

Adsorption from Diluted and Aged Stannic Chloride Solutions

The two obvious methods of increasing the hydrolysis of the standard stannic chloride solution used in the above-mentioned experiments were to dilute it and to age it. Accordingly a fresh 30° Bé. stannic chloride solution (362 gm. per litre) was made up as a reference solution and part of it was diluted to 22° Bé. (245 gm. per litre). Another 30° Bé. stannic chloride solution, which was about five months old, was used as the aged solution. Samples of Chinese silk crêpe were prepared exactly as before (the supply of Japanese silk had been exhausted and no more could be obtained at the time), and weighted in the above-mentioned solutions both in the dry and water-saturated condition for various periods of time as shown in Table V.

TABLE V

EFFECT ON WEIGHTING OF AGING AND DILUTING THE 30° BÉ. STANNIC CHLORIDE SOLUTION

Condition of samples before weighting	Time of immersion in stannic chloride solution, min.	% weighting		
		Fresh 30° Bé. solution	Aged 30° Bé. solution	Fresh 22° Bé. solution
Dry	2.5	5.8	7.6	8.3
Dry	5.0	—	—	9.8
Wet	1.0	8.7	8.8	8.6
Wet	2.5	12.1	—	9.3
Wet	60.0	13.2	13.1	9.8

The pH of the fresh 30° Bé. solution was 0.46, that of the aged, owing to slow hydrolysis, was 0.23. It is seen that in 2.5 min. dry silk picks up 5.8% of weighting from the fresh solution, compared with 7.6% from the

aged solution and 8.3% from a much more dilute solution, although the last result is undoubtedly partly accounted for by the fact that the silk would swell more~ rapidly in the more dilute solution. Little difference can be noted in the results for saturated silk in the two concentrated solutions. It is rather remarkable that silk in this condition picks up virtually as much weighting in one minute from a 22° Bé. solution as it does from a much more concentrated solution, since, in this case, the "swelling" factor is completely eliminated. These results show conclusively that, other conditions being equal, the rate of adsorption of stannic chloride by silk fibroin increases with the degree of hydrolysis of the stannic chloride solution.

Hydrolysis of Stannic Chloride Solutions

It has been tacitly assumed above that silk adsorbs tin from stannic chloride solutions as stannic chloride, since Coughlin found that the ratio of tin to chlorine in the weighting bath does not change. However, this is still an assumption, since no investigator has been able to confirm the presence of any appreciable quantity of stannic chloride in its aqueous solutions (8,21). The hydrolysis of stannic chloride solutions has been investigated by Foster (7), Carstanyen (17, p. 440), Kohlrausch (13, p. 273) and von Kowalewsky (14) and more recently by L. Smith (21), Milda Prytz (19) and Guéron (8). The work of these investigators shows that the rate of hydrolysis of these solutions increases rapidly with dilution and temperature, but is very slow in a solution of the concentration employed by us. However, no completely satisfactory mechanism for the hydrolysis is suggested. It is generally agreed that tin exists in the solution as a complex anion or cation or both. The solutions, of course, are all acid owing to partial hydrolysis, and Smith finds that fresh concentrated solutions contain more Cl^- ions than H^+ ions, which tends to show the presence of positive tin complexes. Guéron concludes, from studies of Raman spectra, that solutions more concentrated than 0.5 molar contain very few molecules of stannic chloride but large numbers of $SnCl_6^{--}$ ions as well as positive tin ions such as Sn^{++++}, $SnCl_3^+$, $SnCl_3OH$, $SnCl_2OH^+$ etc. Milda Prytz finds, from potential measurements in dilute solutions (0.01 to 0.1 molar), that the number of Sn^{++++} ions present varies directly with the concentration of stannic chloride when the Cl^- concentration is kept constant, and that, accordingly, no complex exists containing more than one tin atom. Guéron, on the other hand, considers that $SnCl_6^{--}$ ions can be formed in two ways, *viz.*

$$(1) \quad 3\,SnCl_4 \longrightarrow Sn(SnCl_6)_2$$
$$(2) \quad 3\,SnCl_4 + 2\,H_2O \longrightarrow SnO_2 + 2\,H_2SnCl_6$$
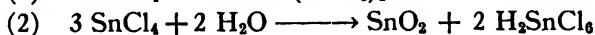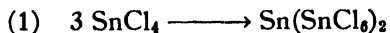
It is impossible, at present, to reconcile these results and theories with the fact that neither the tin-to-chlorine ratio nor the pH of a stannic chloride solution changes during weighting. The specific adsorption of any one tin complex by the silk, except stannic chloride (or a polymer thereof, *e.g.* $Sn(SnCl_6)_2$) would obviously upset the original tin-to-chlorine ratio in the

main body of the weighting solution. Hence, we must conclude from existing evidence that if stannic chloride or $Sn(SnCl_6)_2$ does not exist in appreciable concentration in aqueous stannic chloride solutions, a mixed adsorption of various complexes such as $SnCl_4$, $SnCl_3OH$, $SnCl_2OH^+$, $SnCl_6^{--}$, H_2SnCl_6, $SnCl_5OH^{--}$, etc. must result in a purely fortuitous removal of SnCl from the weighting solution in the approximate ratio of Sn:4 Cl.

The fact that concentrated solutions of stannic chloride contain large quantities of $SnCl_6^{--}$ ions may well explain the shift from positive to negative adsorption of tin that silk exhibits (4), as the concentration of the stannic chloride solution is increased. If $SnCl_6^{--}$ is not adsorbed (or is negatively adsorbed) by silk, and the concentration of $SnCl_6^{--}$ increases at the expense of other tin complexes as the concentration of the stannic chloride is increased in an aqueous solution (which seems evident from Guéron's work), then it would be expected that silk would show a maximum adsorption at some particular concentration of stannic chloride and decreasing adsorption on either side of this critical concentration.

Effect of Temperature and Various Salts on Hydrolysis

In concluding this paper the results of some experiments will be presented which show how various changes in the conditions of hydrolysis affect the weighting retained by silk.

Since the hydrolysis of stannic chloride is hastened both by increase of temperature and the addition of coagulating salts (8) and retarded by hydrochloric acid, and sodium and potassium chlorides, it was decided to find out what effect these factors would have when applied to the hydrolysis of the stannic chloride adsorbed by silk which had come to equilibrium with a stannic chloride solution of 30° Bé.

Saturated samples of Chinese silk crêpe were weighted in the usual manner, hydrolyzed in duplicate under different conditions as specified below, then rinsed well under running tap water and finally dried and weighed. The stannic oxide in the samples was determined by igniting them to constant weight and subtracting the ash of the silk itself. Then,

$$\frac{\text{corrected weight of ash} \times 100}{\text{dry weight of original sample}} = \text{percentage stannic oxide in sample.}$$

The difference between the percentage weighting and the percentage stannic oxide in a sample represents the water present. This is expressed in Table V as a percentage of the total weighting. Thus

$$\frac{(\text{percentage weighting} - \text{percentage stannic oxide}) \times 100}{\text{percentage weighting}} = \text{percentage water in the weighting.}$$

The complete results are tabulated in Table VI.

TABLE VI

EFFECT OF VARIATIONS IN THE CONDITIONS OF HYDROLYSIS

Conditions of hydrolysis	% weighting in samples	% stannic oxide in samples	% water in weighting
Distilled H$_2$O at 25° C.	12.7	–	–
Distilled H$_2$O at 100° C.	11.4	–	–
Distilled H$_2$O at 25° C.	13.9	13.0	6.5
Distilled H$_2$O at 85° C.	13.6, 11.5	12.7, 10.6	6.6, 7.8
Distilled H$_2$O at 100° C.	11.5, 11.3	10.8, 10.8	6.1, 4.4
$\frac{1}{10}$N Na$_2$SO$_4$ solution	16.8, 16.0	–	–
$\frac{1}{10}$N (NH$_4$)$_2$SO$_4$ solution	16.4	14.8	9.8
$\frac{1}{10}$N ZnSO$_4$ solution	15.4	14.0	9.1
10% solution CaCl$_2$	7.5, 6.3	–	–
10% solution KCl	5.7, 5.1	–	–

It is seen that an increase in the temperature of the hydrolyzing bath decreases slightly the stannic oxide retained by the silk, although the rate of hydrolysis of the stannic chloride solution adhering to the samples is greatly increased, as shown by the precipitate of stannic oxide which appears immediately when the samples are plunged into the hot water. Evidently the increased swelling and increased rates of diffusion of the various tin complexes at the higher temperature more than counteract the influence that this increased rate of hydrolysis would be expected to exert, *i.e.*, to cause more tin to be entrapped in the silk pores as stannic oxide and thus produce a higher weighting.

The salts that retard or repress the hydrolysis of stannic chloride, *viz.*, sodium chloride, potassium chloride and calcium chloride, produce a lower weighting when added to the hydrolyzing bath, as would be expected. Furthermore, those salts which cause coagulation and precipitation of dilute stannic chloride solutions (*i.e.* of a positively charged stannic oxide sol (Guéron, Weiser)) produce a weighting higher than normal, as would be expected, since the stannic oxide particles have less time to diffuse out of the silk pores before they are coagulated and precipitated.

The percentage stannic oxide in weighted silk is seen to be always less than the percentage weighting, as has been noted by Coughlin and by Chinn and Phelps (4). They considered the difference to be due to water adsorbed by the silk, but it is obvious that it is water adsorbed by the stannic oxide retained in the silk pores which cannot be driven off by heating at 100° C. Thus L. Schaffner (24, pp. 202, 203, 213-215) found that the α-oxide retains 8% of water at 100° C. and the β-oxide about 12%. The values obtained by the writers are of the same order of magnitude as these figures. The samples hydrolyzed at 100° C. would be expected to have the lowest water content, since Weiser shows that the β-oxide is formed by the hydrolysis of stannic chloride at elevated temperatures. The stannic oxide precipitated in the pores with the aid of the coagulating SO$_4$$^{--}$ ion retained the greatest amount of water.

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THE DETERMINATION OF SULPHUR IN WOOL[1]

By P. Larose[2] and A. S. Tweedie[3]

Abstract

A modification of Pregl's micromethod for the determination of sulphur in organic compounds has been found to be satisfactory and convenient when applied on a macro scale to wool.

The investigation of various methods of cleaning the samples shows that the best results are obtained when the wool wax is extracted with a solvent before washing with water. It is shown that a treatment with dilute hydrochloric acid is not necessary in preparing the sample.

Three different procedures have been followed in determining the dry weight of the sample and the differences in the results are discussed. Results obtained by the new method are compared with those obtained by other recognized methods, and the agreement with the results of the Benedict-Denis-Barritt method is shown to be very good.

Introduction

The predominant role of sulphur in wool is shown clearly by the work of Astbury, Speakman and others. Some of the physical and chemical properties of wool have been attributed to its sulphur content. In view of this the determination of sulphur in wool is important. A number of methods have been proposed and employed for this determination. Although the results obtained by the use of some of these methods are claimed to be satisfactory, the writers wish to describe a new method that has certain advantages over the others.

Method

The method is a modification of Pregl's method for the microdetermination of sulphur in organic compounds. It was developed in 1926 by A. Cambron, of the National Research Laboratories, Ottawa, for the determination of sulphur in organic compounds such as the xanthates. The Pregl method was tried on a macro scale and found unsatisfactory for these compounds, and the modifications described here had to be made before satisfactory results could be obtained. It was suggested that Cambron's method might be a convenient one for determining sulphur in wool. Preliminary experiments made in 1931 showed that the method was satisfactory for this purpose, but the results obtained at that time were too meagre to warrant publication. During the past year a number of determinations were made with this method, and a number of the samples were also analyzed by the Carius and the Benedict-Denis methods for the purpose of comparison.

The method consists essentially in burning the material in a stream of oxygen, passing the products of combustion over platinum and absorbing them in hydrogen peroxide solution. The sulphur was determined as barium sulphate in the usual way.

The apparatus used is shown schematically in Fig. 1. *E* is a quartz tube 24 in. long*. A portion of its length is heated in a furnace, *F*. *H* and *K* are the platinum catalysts which oxidize the sulphur dioxide to sulphur trioxide. *H* is the platinum contact star of a standard type for combustion tubes. *K* is a roll of platinum gauze.
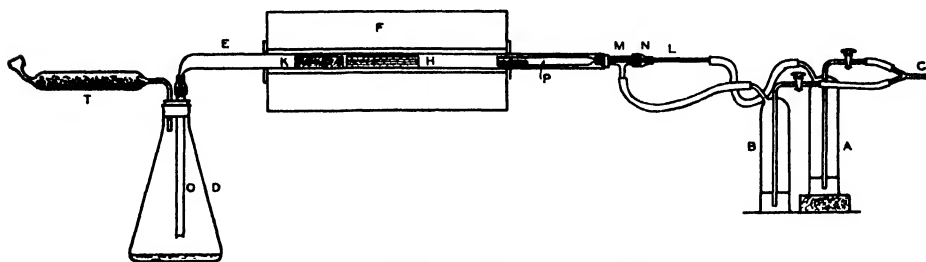
FIG. 1. *Apparatus for the determination of sulphur in wool.*

One end of the quartz tube is sealed to a small tube at right angles to it. This small tube fits into a somewhat larger delivery tube, *O*, that passes through the cork of the absorption flask, *D*. The two tubes are held together by a short piece of rubber tubing. To the absorption flask, *D*, is connected a tube, *T*, filled with small pieces of glass rod; 25 cc. of 5% hydrogen peroxide is placed in the flask, and 5 cc. in the tube *T* so as to wet thoroughly the small pieces of glass. The end of the tube *O* is adjusted to a height of about one inch above the surface of the liquid.

The sample of wool is placed in the quartz tube, *P*, of a diameter slightly smaller than that of the tube *E*. Tube *P* is sealed to a tube *L* of smaller diameter. A tube *M*, concentric with *L*, is joined to *L* by means of a short length of rubber tubing, *N*. Both tubes pass through the cork closing the end of the tube *E*. *M* carries a side tube connected to a bubbler, *B*, while *L* is connected to the bubbler *A*. A stream of oxygen is introduced at *C*. It passes through the bubblers and enters the combustion tube through the tube *P* and through the annular space between *M* and *L*. The purpose of the bubblers *A* and *B* (containing water) is to permit adjustment of the gas stream in both inner and outer tubes. During combustion the gas is bubbled through *A* at a rate of about one bubble every two seconds, while that through *B* is slightly more rapid.

The purpose of the outer stream is to prevent any back flow of the products of combustion, some of which are liable to cause an explosion if combustion is rapid. This arrangement and that of the absorption flask are the modifications made to Pregl's apparatus. Because of these modifications the sulphur trioxide collects as a cloud over the surface of the solution and is slowly absorbed by it. The tube *T* insures complete absorption.

At the beginning of a determination, the furnace is heated and when the temperature at the centre is 650° C. the wool sample, wound with a short piece of platinum wire to keep it in a fairly compact roll, is introduced into the end

* *As the apparatus was drawn to scale, the dimensions of the other parts can readily be estimated.*

of the tube P, which is then adjusted so that its end is just inside the furnace. As the wool burns, the tube L is gradually pushed forward until the tube P is virtually in contact with the platinum H. The wool is entirely carbonized after about 20 min. in the combustion tube. The combustion is continued for a further 20 min. This is usually sufficient to burn off the carbon completely. Only a small amount of ash is left in tube P. The quartz tube, E, is then disconnected at its inlet end, the furnace is opened and the tube is taken out to cool. Care must be taken during this manipulation that any condensed acid in the cool part of the tube does not run back into the heated section and vaporize. When the tube has cooled sufficiently, it is washed with distilled water and the washings are run into the flask D. The contents of the tube T is also washed carefully into D. Then the solution is boiled to decompose the hydrogen peroxide and to reduce the volume of liquid. The ash remaining in the tube P is washed into a beaker and heated with dilute hydrochloric acid to dissolve as much of it as possible. Any undissolved portion, always small and occasionally nil, is filtered off and the solution added to that in flask D. The solution is then transferred to a beaker and twice evaporated to dryness with hydrochloric acid to eliminate nitrates which may interfere with the barium sulphate precipitation. This evaporation to dryness was not carried out when the method was first applied, but, as will be shown later, the results so obtained are too high owing to interference of nitrates. The barium sulphate is determined in the ordinary way. A hot solution of 3% barium chloride is added drop by drop to the hot sulphate solution acidified with hydrochloric acid. With a sample of 0.2 to 0.3 gm. of wool excellent results were obtained by precipitating from a volume of about 40 cc. A few drops of acetone was added to the sulphate solution just before the addition of the barium chloride to facilitate the formation of a crystalline precipitate. The precipitate was allowed to stand for one hour before filtering.

Blank determinations were carried out at regular intervals. The value of the blank depended entirely on the hydrogen peroxide used, and was constant for any one lot.

In certain cases the ash remaining in the tube P was analyzed separately for sulphur.

Experimental

Cleaning of Sample

Experiments showed that the most effective of the methods tried for cleaning the sample was to extract it in a Soxhlet apparatus and then wash it with distilled water.

Table I shows the sulphur content of samples cleaned by various procedures. The effect of thiophene and carbon disulphide in the benzene was investigated in order to determine whether sulphur-containing impurities in the solvent might be retained by the wool and result in erroneous values for the sulphur content.

It is evident that cleaning of the wool is best carried out by first extracting the wax with a solvent, and that the particular solvent or its purity is not of great importance. For economy, petroleum ether was used as the solvent for

all other determinations. The final procedure adopted was to extract the wool with petroleum ether in a Soxhlet for two hours or longer. This was followed by washing with warm 0.1% saponin solution and then with distilled water. After drying, the wool was teased out by hand and all extraneous matter not removed in the washing, such as small bits of skin, leaves, straw

TABLE I

THE EFFECT OF VARYING THE WASHING PROCEDURE

Procedure	Per cent sulphur	Mean, %
*Low ¼ Leicester (Alberta)**		
Washed in purified ethyl ether, 0.1% saponin solution and water, *A*	3.60 3.60 3.66 3.63	3.62
A re-extracted with ethyl ether	3.66 3.66	3.66
A re-extracted with ethyl ether and washed with water	3.64 3.68	3.66
A re-extracted with benzene (Merck's pure)	3.68 3.66	3.67
A re-extracted with benzene and washed with water	3.62 3.66 3.69	3.66
Washed with 0.1% saponin solution and water, *B*	3.58 3.55 3.60 3.54 3.59	3.57
Extracted with benzene (thiophene free),	3.67 3.64 3.64 3.59	3.64
Mixture of *A* and *C* re-extracted with benzene + 0.05% thiophene, *D*	3.63 3.64 3.63	3.63
D after washing in 0.1% saponin solution and water	3.64 3.60 3.62	3.62
Mixture of *A* and *C* re-extracted with benzene + 0.05% carbon disulphide	3.63 3.64 3.62 3.62	3.63

Percentage of sulphur in the ash varied between 0.5 and 1.3% of the total sulphur; the mean for all determinations was 0.8%.

TABLE I—*Concluded*

THE EFFECT OF VARYING THE WASHING PROCEDURE—*Concluded*

Procedure	Per cent sulphur	Mean, %
Alberta fine Merino wool (1934 spring 64-66's)†		
Washed in bulk in benzene, 0.1% saponin solution and water, *A*	3.53 3.85 3.58 3.75 3.66 3.65	3.67
A extracted with pure ethyl ether	3.88 3.87	3.88
A extracted with benzene	3.84 3.90 3.92 3.89	3.89
Washed in purified ethyl ether, 0.1% saponin solution and water, *B*	3.88 3.88 3.81 3.92 3.87	3.87
Washed in unpurified ethyl ether, 0.1% saponin solution and water, *C*	3.87 3.88 3.92 3.86 3.89	3.88
A re-extracted with petroleum ether and washed in running water	3.90 3.87	3.89
Hampshire, ⅜ staple wool		
Extracted with petroleum ether, washed in 0.1% saponin solution and with water	3.31 3.31 3.29	3.30
Re-extracted with benzene and washed with water	3.33 3.30 3.31	3.31

†*Mean value for ash sulphur was 1.1% of total sulphur.*

In obtaining the above results, evaporation to dryness, to remove nitrates, was not carried out. All results are given on a dry-weight basis.

and tangled wool, was picked out. The wool was then re-extracted with petroleum ether, with alcohol and finally washed for five to six hours in warm running distilled water. Although tests showed that the extraction with alcohol did not appreciably affect the results, it was preferred to carry it out as a safety measure.

One of the wools was also soaked in dilute hydrochloric acid $(0.01\ N)$ for 24 hr., a procedure claimed by Marston (4) to be necessary. In confirmation of the results of Barritt and King (3), this procedure made no appreciable difference in the sulphur content found, as shown in Table II.

TABLE II

THE EFFECT OF PRETREATING WITH HYDROCHLORIC ACID

Procedure	Sulphur, %
No soaking in hydrochloric acid	4.12
Soaking in $0.01N$ hydrochloric acid, 24 hr.	4.08

Welsh wool (ref. X31) prepared according to standard procedure.

According to Marston, equilibrating with dilute hydrochloric acid removed inorganic sulphur, which is present as sulphate in appreciable quantities in many cases. In the combustion method this sulphur would remain in the tube as an ash. It will be noted that wherever the sulphur in the ash was determined separately, it was only about 1% of the total sulphur, so that large variations found in the sulphur content of various wools cannot be attributed to this factor.

Drying of Sample

Following the cleaning operations, the wool sample was dried to constant weight in a drying oven at 105° C. (two hours is generally sufficient), the wool being weighed without removal from the oven. This differs from the procedure followed by some other workers, whereby the wool is conditioned and the moisture content determined on a representative sample, the other samples employed for the sulphur determination being weighed in the conditioned state. However, tests carried out by the two methods showed that the dry weight obtained in the oven was slightly high (about 0.4%) compared with the dry weight calculated from the moisture content determined by the method of Barritt and King (2). This resulted in an apparent lowering of the sulphur content by 0.014% (actual content).

Tests also showed that heating at 105° C., for the time necessary to dry the sample, actually lowered the sulphur content by less than 0.04%. This lowering varies with different wools and may be nil in some cases. This seems to have been realized by other workers; for example, Barritt and King state (2) that they adopted the method of weighing the conditioned sample "to guard against the possibility that wool on drying out may lose volatile sulphur compounds, though this from experiments carried out appears to be improbable." It is likely that the particular wool that they investigated was of a type that gave the smaller difference.

The drying of the sample in the oven eliminates the necessity of conditioning it. This procedure is of advantage when the results are desired

in as short a time as possible and where conditioning facilities are not available. When utmost accuracy is required, it might be preferable to follow the method in which a regain determination is made on a separate sample. However, the error introduced by drying the sample in the oven is so small that the writers have considered this procedure satisfactory for general purposes, especially since the error can be largely reduced by applying a mean correction to the figures obtained. This mean correction, obtained from determinations on five different wools, is $+0.03\%$ actual sulphur.

TABLE III

THE EFFECT OF VARYING THE DRYING PROCEDURE

Procedure	Per cent sulphur					
	Leicester	South-down	N.Z. 40's	N.Z. 60's	Cheviot	Welsh X31
Standard, (a)	3.47_0	3.80_0	3.11_5	3.55_0	3.83_5	4.12_5
Conditioned sample, regain determined in large drying oven, (b)	3.48_5	—	3.12_0	3.58_5	3.87_5	4.13_5
Conditioned sample, regain determined by method of Barritt and King, (c)	3.50_0	3.81_5	3.13_5	3.59_5	3.89_0	4.15_0
Difference between (c) and (b)	0.01_5	—	0.01_5	0.01_0	0.01_5	0.01_5
Difference between (c) and (a)	0.03_0	0.01_5	0.02_0	0.04_5	0.05_5	0.02_5

The difference between (c) and (b) is due to the difference in the determined moisture content. It may be observed that the difference is fairly constant. The difference between (b) and (a) corresponds to the loss in sulphur during the drying, while the difference between (c) and (a) is the total error introduced by the drying method employed, and it has a mean value of 0.03%.

Elimination of Nitrates

It has been stated earlier in the paper that it was found necessary to evaporate the hydrogen peroxide solution to dryness with hydrochloric acid in order to eliminate nitrates. This evaporation to dryness was carried out twice for each sample. Table IV gives the results obtained with various wools when this evaporation

TABLE IV

EFFECT OF EVAPORATION OF THE HYDROGEN PEROXIDE SOLUTION TO DRYNESS

Wool	No evaporation, per cent sulphur	With evaporation, per cent sulphur
Alberta Merino	3.88	3.75
Cheviot, ¼ staple	3.92	3.83
Romney, L-¼	3.75	3.70
Hampshire, ⅜	3.30	3.20
Kempy	3.59	3.45
Leicester, L-¼	3.59	3.47

Mean difference, 0.11. .

was not carried out, as compared with those obtained on double evaporation. It will be seen that, on the average, the results are 0.11% too high when the nitrates were not removed.

Comparison of Methods

Various wools were analyzed for sulphur by the Benedict-Denis (Barritt's modification (1)), the Carius, and the combustion methods for purpose of comparison. The Wool Industries Research Association analyzed and supplied five of these wools and also analysed two wools that the writers had sent them. Table V shows a summary of the results obtained.

TABLE V

COMPARISON OF METHODS

Sample	Combustion	Carius	Benedict-Denis	Wool Industries Research Association
Leicester L-$\frac{1}{2}$	3.47	3.46	—	
Southdown	3.79	—	3.79	
Western Australian Merino	3.57	3.58	3.53	3.73 (Benedict-Denis-Rimington)
Australian 70's	3.65	3.63	---	3.73 (Benedict-Denis-Barritt)
Welsh	4.02	3.92	3.97	3.92 (Carius)
Scotch Black Face	3.26	3.28	3.21	3.10 (Benedict-Denis-Rimington)
Welsh $X31$	4.12 (4.15)	4.08	4.00	4.15 (Benedict-Denis-Barritt) 4.14 (Carius)
Suffolk	3.77 (3.80)	—	—	3.80 (Benedict-Denis-Barritt)
New Zealand 36's	3.16 (3.19)	—	—	3.20 (Benedict-Denis-Barritt)

NOTE:—*The figures in brackets are the corrected figures obtained when regain of separate samples is determined in a small drying oven.*

The agreement between the results obtained by the writers with the combustion and the Carius methods is, with one exception, very good. The Benedict-Denis method yielded results that were lower than those of the other two methods by about 0.05% (actual). The discrepancy between the values obtained for the Welsh wool by the Carius and those obtained by the combustion methods has not been explained. The determinations were repeated at various times and always with the same results. In view of the fairly constant difference between the values obtained by the Benedict-Denis and by the combustion methods, it would appear that the value for the Carius determination is, for some unknown reason, too low, although it is in agreement with that furnished by the W.I.R.A., which value was also obtained by the Carius method. Regarding the other values given by the W.I.R.A., it will be seen that there is good agreement for the last three wools. In these three cases the interval between the analyses carried out by the writers and those of the W.I.R.A. was comparatively short, but with the other wools the situation was different. The samples of Australian Merinos, for example, were more than one and one-half years old when analyzed by the writers, while the sample of Welsh wool was three years old or more.

The value given for the Scotch Black Face sample was determined by the Rimington modification of the Benedict-Denis method and this, according to Barritt (1), gives results 0.1 to 0.15% (actual) too low.

In order to point out the agreement obtained in several determinations on the same wool, typical sets of values for two different wools are given in Table VI.

The method was checked also by carrying out the determination with pure cystine. Found: 26.58, 26.50, 26.55, 26.60, 26.46, 26.58, 26.67%. Mean, 26.56%. Theoretical, 26.69%.

As 0.0001 gm. of barium sulphate in the determinations on cystine was equivalent to 0.05% actual sulphur content, the above figures are subject to an error of at least ±0.05%.

TABLE VI

TYPICAL RESULTS

Wool	Per cent sulphur	Mean %
Leicester $\frac{1}{4}$ Blood	3.50	
	3.45	
	3.45	
	3.48	
	3.46	3.47
Cheviot	3.82	
	3.85	
	3.84	
	3.82	3.83

Advantages of the Method

Several methods have been proposed that would give satisfactory results for the determination of sulphur in wool. Of these the most widely used have been the Carius and the Benedict-Denis methods. A bomb method (1) has apparently also given good results. An electrolytic method has been used by Mossini (5).

A general review of the methods in use up to 1926 is given by Barritt and King (2). Up to that time they considered that the Carius method was the most satisfactory. However, the Carius method is generally recognized as being too laborious for ordinary purposes. The Benedict-Denis method is not easy to carry out, and the writers have found that great care is required to obtain concordant results. Complete and ready solubility of the ignited residue apparently depends on the conditions of ignition. The writers were unable to obtain complete solubility of this residue. This may account for the lower results that they obtained with this method. In the method are introduced metal salts, and these generally interfere in the sulphate precipitation. The bomb method, which makes use of sodium peroxide, is also open to this objection. Moreover, it is not easy to mix the wool thoroughly with the peroxide. A special apparatus is required and the removal of iron from the solution which is generally necessary is an added complexity. In the combustion method no foreign substance is present. There is no mixing to be done. The method is rapid and requires very little care apart from that generally necessary in analysis. Marston (4) has stated that sulphur estimation in organic materials is not easy, and that complete oxidation is well nigh impossible without a wet ashing process. The good results obtained by the combustion method do not bear out this contention.

If one may judge from the results given by Barritt (1) the deviation of the individual results is larger for the bomb method than for the Benedict-Denis method carried out with the nitric acid, but the writers have found the results of the combustion method to give a deviation even less than that given by the Benedict-Denis method.

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THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL AT LOW SURFACE CONCENTRATIONS[1]

By Melville J. Marshall[2] and Alexander S. MacInnes[3]

Abstract

The differential heat of adsorption of oxygen on activated cocoanut charcoal has been measured over the low concentration range to 14 micromoles per gram, by means of an improved ice calorimeter and a new charcoal bulb, in which oxygen is introduced into the middle of the charcoal mass. At zero concentration, a heat of adsorption of 129.0 kcal. per mole of oxygen was found, dropping to 72.0 kcal. at approximately 6.0 micromoles per gram. The initial heat of adsorption is much higher than the highest value that has been obtained previously. This indicates that the plain charcoal bulb previously used permitted loss of heat from the calorimeter; consequently, the values for the initial heats of adsorption were low. The theoretical significance of the high initial heat is discussed briefly.

Introduction

The differential heat of adsorption, at zero concentration, of oxygen on activated wood charcoal was found by Keyes and Marshall (5), using an ice calorimeter, to be 72.0 kcal. per mole. Later, Marshall and Bramston-Cook (7), using a larger quantity of activated cocoanut charcoal and an improved ice calorimeter, obtained the value 89.6 kcal. With the exception of these initial heats, the values obtained in the two investigations agreed reasonably well. This unusually high initial heat value made it of some interest to investigate in more detail the heats of adsorption over the low concentration range.

In 1934, Harold H. Herd (4), working in this laboratory, obtained with an improved apparatus an initial heat of adsorption of 95.3 kcal. In 1935, Harry Lotzkar (6), continuing the work of Herd, made four series of determinations. He obtained, for the initial heats, values varying from 75.3 to 89.3 kcal. These varying results led to the conclusion that either the more active part of the charcoal surface varied considerably after each outgassing, or some uncontrolled error still existed in the method of measuring the heat evolved. This variation could not be attributed to the existence of a slow chemical reaction following the apparently complete heat evolution, as the heat loss could be reproduced after about one hour for initial gas adsorptions. At higher concentrations the time of heat evolution is greater and the error should consequently be larger. In spite of this, the variation of heat of adsorption was most marked for the heat evolution resulting from the first addition of oxygen. Consequently, it was thought possible that this oxygen might be adsorbed entirely in the upper layers of the charcoal, and that this resulted in a relatively high temperature increase at a point in the charcoal where heat losses by radiation and convection would be most likely to occur.

To avoid this possibility in the present investigation, the silica bulb was altered in such a way that the oxygen could be introduced into the middle of the carbon mass instead of at the top as formerly (7). Smaller increments of oxygen were added, and the investigation was confined to a concentration range extending to 14 micromoles per gram.

Experimental

In the previous investigation (7) the charcoal was contained in a plain silica bulb joined to the remainder of the apparatus by means of a silica tube about 1.3 cm. in diameter. The charcoal was outgassed and the oxygen admitted through this one tube. The new bulb is shown in Fig. 1. The

FIG. 1.

The charcoal bulb.

small silica tube, B, was fused into the charcoal bulb in such a way that it would not, by increasing the effective diameter, interfere with the insertion of the bulb into the calorimeter. The gas escaped from B into the charcoal through three small holes, each about 1 mm. in diameter. One hole was situated at the lower end of the tube B, and the other two were situated on opposite sides of the tube, as shown at D. In this way it was hoped to cause the oxygen to enter the charcoal at three points, and so obtain better distribution. The charcoal level is indicated by the dotted line at C. The highest hole was kept well below this level to ensure that none of the initial heat was generated on the upper surface of the charcoal. Tube A was connected, as before, by a short wide tube to the diffusion pump, in order to minimize resistance to the flow of gas at low pressures while the charcoal was out-gassed. Tube B was connected directly to the gas pipette, for introduction of the oxygen. Graded silica-to-Pyrex seals were used for connecting both tubes to the remainder of the apparatus. The platinum lining of the original bulb was removed, as its advantages were doubtful, and the experimental difficulty of retaining it was considerable.

In the previous experiments (7), the space C in the calorimeter was filled with ice, and the voids between the pieces of ice were filled with distilled water. The use of water has since been found to be a disadvantage, as the ice floated to the top as it melted. This left the bottom of the calorimeter unprotected. In this investigation no water was used, but the ice was disturbed from time to time with a probe, and more ice was added when needed. One drawback to this arrangement was that the ice would melt away from the vertical part of the mercury capillary, and heat would flow down the mercury into the calorimeter. This was prevented by bending the capillary in a single horizontal loop, so that it encircled the neck of the calorimeter just above the rubber stopper, and thus ensured that the ice remain, owing to gravity, in contact with the lower part of the capillary.

A tendency of the mercury to stick to the walls of the capillary tube *A* (7) is responsible for some of the variation in the heat loss. In order to avoid this as much as possible, the capillary tube was wetted with water before the mercury was introduced. This decreased the heat value of the capillary per centimetre by 0.53% and caused the heat loss readings to be more nearly uniform, though some sticking of the mercury was still noticeable.

Mercury cutoffs replaced the stopcocks used previously (7). The two-way stopcock on the gas pipette *J* was of necessity retained, but it was protected by a mercury cutoff. As all adsorptions were made at very low pressures, the manometer *H* was removed and the small McLeod gauge replaced by one with a volume ratio of 10^{-5}.

The charcoal weighed 25.634 gm. and was identical with that used in the earlier investigation (7). With the exception of the changes mentioned previously, the method of operation of the calorimeter and the treatment of the charcoal were unaltered. In the present investigation the ice mantle was used for three weeks at a time, and was discarded only because of the necessity of outgassing the charcoal for a new series of determinations.

Results

The treatment of the results was similar to that previously followed (5, 7). The summation of the increments of heat, *q*, evolved in calories per gram of charcoal was plotted against the summation of the increments, *c*, of gas adsorbed in moles per gram of charcoal. The slope of the curve dq/dc at a point gives the differential heat of adsorption, *Q*, in calories per mole of oxygen at that point.

The experimental values of *c* and *q* are given in Table I. In Series 2 very small amounts of gas were employed, in order to approach zero concentration as closely as possible. The first value in this series falls on the *q*–*c* curve of

TABLE I

EXPERIMENTAL HEAT VALUES

Series 1				Series 2	
$c \times 10^6$	q	$c \times 10^6$	q	$c \times 10^6$	q
1.29	0.125	7.84	0.598	0.583	0.0673
2.70	0.229	9.91	0.746	1.149	0.1202
4.29	0.345	11.92	0.893	1.915	0.1825
6.05	0.467	13.82	1.031		

Series 1, while the second and third values lie slightly higher than the curve. However, the two series give the same initial heat value, and continue to agree exactly to about 0.6 micromoles per gram. It is by no means certain that complete agreement for the intermediate values is to be expected, as a small variation in the number of the most active spaces might easily occur at successive outgassings. If it is assumed that the heat evolution from each

of the most active spaces does not vary under these conditions, then variation
in the number of spaces would not affect the initial heat of adsorption, but
would affect the shape of the curve between the initial heat and the constant
heat of 72.0 kcal.

The values of Q and c obtained from the q–c curve are given in Table II,
and plotted in Fig. 2. Points are also shown for the values obtained by
Herd (4), and for the values obtained by Marshall and Bramston-Cook (7),
although no curves are drawn.

TABLE II

VARIATION OF DIFFERENTIAL HEATS OF ADSORPTION WITH CONCENTRATION

$c \times 10^6$	Q, kcal.	$c \times 10^6$	Q, kcal.	$c \times 10^6$	Q, kcal.
0.0	129.0	1.0	80.3	2.0	74.2
0.2	119.0	1.2	77.4	3.0	73.5
0.4	105.1	1.4	74.8	6.0	72.0
0.6	94.4	1.6	74.8	14.0	72.0
0.8	86.4	1.8	74.8		
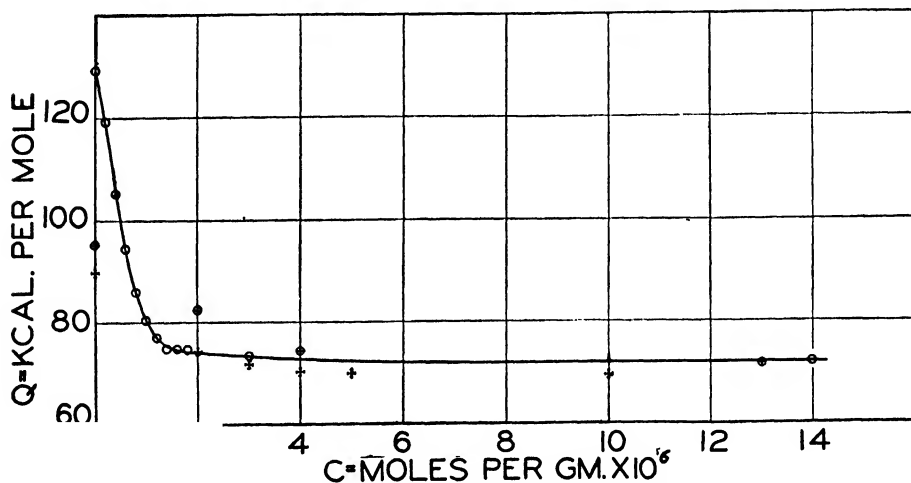
FIG. 2. $\circ$, MacInnes; $\bullet$, Herd; $*$, Bramston-Cook.

Discussion

It will be noticed that the present results show a marked increase only for
the initial heats of adsorption. For the higher concentrations they agree
very well with the values obtained by Herd (4), while those obtained by
Marshall and Bramston-Cook (7) are only slightly lower. The fact that
only the initial heat is affected by the alteration in the silica bulb seems to
verify reasonably well the previous assumption that a certain fraction of the
initial heat had escaped from the calorimeter in the earlier investigations.
This confirms the observation of Bull, Hall and Garner (2) that the initial

quantity of oxygen added is adsorbed almost completely in the part of the charcoal with which it first comes in contact. They found that this led to considerable error for the initial heat when a thermocouple calorimeter was used. Until the above-mentioned difficulties with the initial heat were encountered, the present writers were of the opinion that this effect would produce no error whatever with the ice calorimeter, as the ice mantle extended a considerable distance above the level of the charcoal, and it was considered adequate to absorb all the heat, no matter where the heat was liberated.

The constant heat of adsorption of 72.0 kcal. agrees with the original value obtained by Keyes and Marshall (5) as well as with that obtained by Herd (4) in this laboratory. This value is probably more accurate than the value of 70.0 kcal. obtained by Marshall and Bramston-Cook (7). Since Bull, Hall and Garner (2) also obtain a flattening of the curve in the vicinity of this point, the reality of this constant heat can now be considered to be definitely established. The significance of this constant value is still a matter for speculation.

While the initial heat of adsorption is much higher than that previously obtained, it is still below the high heats of about 200.0 kcal. obtained by Garner and his co-workers (1, 3, 8) at higher temperatures, or the still higher heats which can be calculated on the assumption that the surface bonds are equal in strength to those of an atom of gaseous carbon (3, 5). An exact estimate of a theoretical value for the initial heat of adsorption is not possible at the present time, as neither carbon monoxide nor carbon dioxide is formed at 0° C., and the heats of formation of surface compounds, consisting of oxygen atoms combined chemically with the carbon atoms at the surface in various definite ways, are unknown. In view of these considerations, there is no reason why the initial heat of adsorption should not be greater than 96.4 kcal., the heat of formation of carbon dioxide from charcoal.

The possibilities exist for the formation, on the surface, of complexes corresponding to compounds containing carbon and oxygen in ratios quite unknown in the normal state. Such a complex high in carbon could give rise to the high initial heat of adsorption, while a decrease in the carbon to oxygen ratio, owing to an increase in the oxygen concentration, could give the lower heats of about 72.0 kcal. However, further speculation will be deferred until new pressure equilibrium data, now being accumulated in this laboratory, are available. It is hoped to use the present results, in conjunction with these data, to throw more light on this rather complicated problem.

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THE EFFECT OF PRETREATING WOOD IN AQUEOUS SALT SOLUTIONS ON SUBSEQUENT DELIGNI-FICATION IN SULPHITE LIQUOR[1]

By J. M. Calhoun[2] and O. Maass[3]

Abstract

The pretreatment of spruce wood in various neutral salt solutions was found to retard subsequent delignification in sulphite liquor to an extent depending upon the position of the ions of the salt in the lyotropic series. Increase in the salt concentration increased the effect of pretreatment.

Introduction

Corey and Maass (1) have described the effect of pretreating spruce wood in buffer solutions of various hydrogen ion concentrations on subsequent sulphite cooking. They found that delignification was retarded to an amount depending on the pH of the pretreating solution; the effect was a minimum at pH 5 and increased at lower and higher hydrogen ion concentrations. The explanation offered to account for the phenomena was that an agglomeration of the lignin particles took place, and that this rendered subsequent cooking more difficult.

It has since been found that pretreatment with different buffers at the same pH gives different results. This led to an investigation of the effect of pretreatment with various neutral salt solutions. Although the hydrogen ion concentration of different buffers may change at cooking temperatures in a different manner, evidence is presented which indicates that other factors must be considered before any satisfactory explanation of the pretreatment phenomena can be made.

Experimental

Portions of spruce wood-meal, 40-100 mesh, density 0.34, lignin 29.0%,* with solutions of various salts, were sealed in bronze bombs and heated, at the cooking temperature, in a well stirred glycoline bath for a definite time. The pH of the pretreating solution was checked at room temperature by means of a quinhydrone electrode, before and after heating. The meal was washed free of salt solution, air dried and then cooked in calcium bisulphite liquor containing 5.1% of total, and 1.2% of combined, sulphur dioxide. The resulting pulps were analyzed for both lignin and sulphur.

Discussion

Tables I and II show the effect of pretreating spruce wood with various potassium salts and chlorides arranged in order of the residual lignin content of the pulps. A run without pretreatment and one with pretreatment with

TABLE I

EFFECT OF ANIONS IN PRETREATMENT

Pretreatment: 6 hr., 140° C.; cooking 3 hr., 140° C.

Pretreating solution 1.0 molar	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
No pretreatment	47.4	45.9	1.48	13.4
Pretreated with water only	59.2	47.4	11.8	—
KCNS	68.6	46.6	22.0	4.58
KI	60.2	46.2	14.0	5.32
KBr	60.2	48.0	12.2	—
KNO₃	59.7	47.6	12.1	5.54
KCl	58.6	47.3	11.2	5.98
KH₂PO₄	59.7	49.7	9.95	6.18
K₂SO₄	57.1	48.0	9.10	5.91

TABLE II

EFFECT OF CATIONS IN PRETREATMENT

Pretreatment: 6 hr., 140° C.; cooking 3 hr., 140° C.

Pretreating solution 1.0 molar	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
NH₄NO₃	67.2	43.6	23.6	3.47
NH₄Cl	66.9	44.1	22.8	3.79
SrCl₂	64.4	46.3	18.1	4.23
CaCl₂	63.0	45.7	17.8	—
BaCl₂	63.5	46.6	16.9	4.83
MgCl₂	61.5	47.3	14.2	5.23
LiCl	61.3	48.2	13.1	5.63
NaCl	59.0	47.3	11.7	5.77
KCl	58.6	47.3	11.2	5.98

water only serves as a comparison. The pH of the pretreating solutions in each case was found to be well within the range pH 4 to pH 6 which Corey and Maass (1) have shown to have a minimum effect on pretreatment. Hence, the results obtained cannot be attributed to differences in hydrogen ion concentration of the different salt solutions.

It may be noticed that in almost every case the sulphur content of the lignin varies inversely as the lignin content of the pulps. This indicates that pretreatment hinders sulphonation of the lignin rather than the hydrolysis of sulphonated lignin, although probably both reactions are affected.

The close connection between the observed order of the anions and cations in pretreatment and the lyotropic series is apparent at once. The order of the lyotropic series given by Traube (5) is:

(a) For the hydration of ions:

CNS. < I   < Br   < NO₃   < Cl   < HPO₄   < SO₄
Ba < Sr < Ca   < Mg   ;   NH₄   < K   < Na   < Li
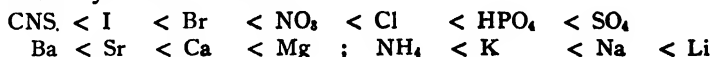
(b) For the swelling of gelatin:

CNS > I   > Br   > NO₃   > Cl   > SO₄

The observed order of the anions in pretreatment is the reverse of that for the hydration of the ions, but the same as that for the swelling of gelatin. This suggests that swelling may play a part in the phenomena.

The order found for the cations in pretreatment does not agree as well with the lyotropic series. The observed order for the alkaline earth metals is the reverse of that for hydrate formation, while the observed order for the alkali metals is the same as the order for hydrate formation. The effect of NH_4^+ is entirely out of proportion to its position in the lyotropic series, although ammonium nitrate has a greater effect than ammonium chloride. This shows the lyotropic effect of the anion. It is believed that ammonium compounds may have a specific action on lignin.

Table III and Fig. 1 show the effect of varying the concentration of potassium thiocyanate in the pretreating solution. The retarding of subsequent delignification increases rapidly with the concentration of the salt, and again it can be seen that the sulphur content of the lignin is inversely proportional to the residual lignin content of the pulp.
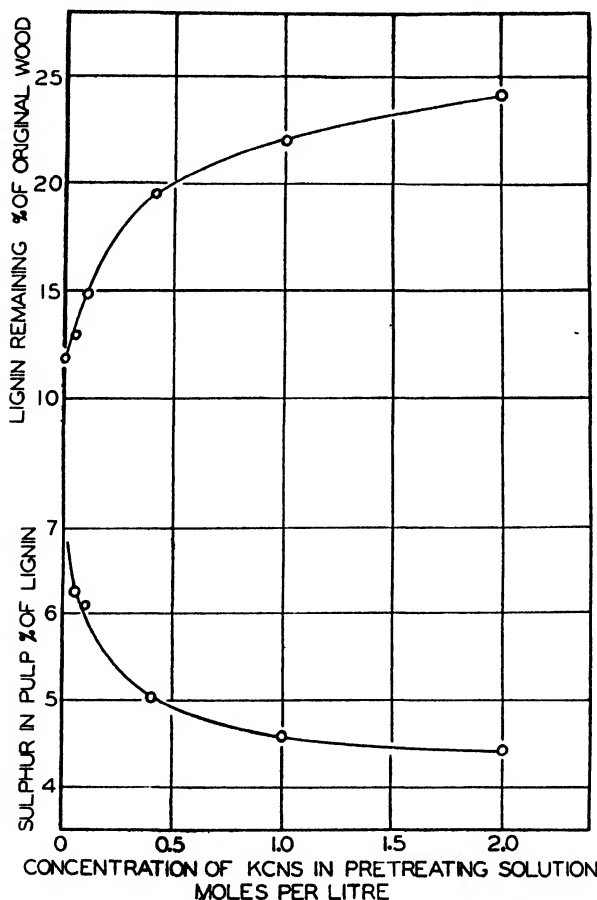
Fig. 1. *Effect of concentration of potassium thiocyanate in pretreating solution on subsequent delignification.*

TABLE III
EFFECT OF CONCENTRATION OF POTASSIUM THIOCYANATE IN PRETREATMENT
Pretreatment: 6 hr., 140° C.; cooking 3 hr., 140° C.

Concentration of KCNS, moles per litre	Yield of pulp, %	Yield of carbohydrate, %	Lignin as % of original wood	Sulphur as % of lignin
0.0	59.2	47.4	11.8	—
0.05	61.5	48.6	12.9	6.26
0.10	63.4	48.6	14.8	6.12
0.40	66.0	46.5	19.5	5.02
1.0	68.6	46.6	22.0	4.58
2.0	70.4	46.2	24.2	4.42

The influence of the lyotropic series on numerous physical chemical properties of solutions and lyophilic colloids has long been known. The explanation of the phenomena in the present case is not so clear. Stamm (4) has shown that the saturated solutions of chloride and potassium salts cause a swelling of wood and other cellulosic materials at room temperature, beyond the normal water-swollen state, in the following order:

$$Zn > Li > Ca > Mg > Mn > Ba > Na > NH_4 > K$$
$$CNS > I > CrO_4 > Br > Cl > NO_3 > SO_4 > CO_3$$
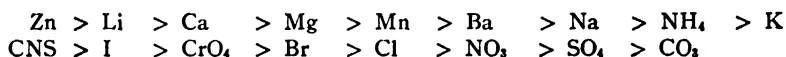
Decrease in the salt concentration decreases the extent of swelling. According to Herzog and Beck (2), saturated solutions cause a peptization or partial solution of cellulose at temperatures above 135° C., in the order:

$$Ca > Ba ; Li > Na > K > NH_4$$
$$CNS > I > Br > NO_3 > SO_4$$
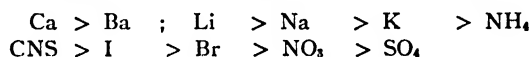
At the present stage of the investigation, it cannot be stated whether swelling or peptization or both play a part in the pretreatment phenomena. It can be pointed out only that the influence of the lyotropic series is similar in all three cases. Any satisfactory explanation must also account for the effect of varying the hydrogen ion concentration of the pretreating solution, as observed by Corey and Maass. It has been shown by Stamm (4) that the swelling of wood is independent of pH except in very alkaline solutions. However, it has been shown here that the problem is intimately connected with the colloidal nature of lignin and cellulose, and it is hoped that work under way will throw more light on the subject of pretreatment and thus indirectly on the mechanism of sulphite pulping.

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THE NATURAL OCCURRENCE OF ACETYL-ORNITHINE[1]

By Richard H. F. Manske[2]

Abstract

The tap-roots of *Corydalis ochotensis* were found to contain a relatively large amount (10%) of an amino-acid, the chemical examination of which disclosed it to be the hitherto unknown *mono-acetyl-d-ornithine*. Although acyl and aroyl derivatives of amino-acids have long been recognized as animal catabolites, such derivatives do not appear to have been previously observed as plant anabolites.

The author has been engaged upon a program of research, the primary object of which is the elucidation of the nature of the alkaloids of a number of plants belonging to the Natural Family Fumariaceae. Some twenty species have been investigated in whole or in part. In many cases, thus far unreported by-products such as sterols, sterolins, alcohols and other neutral substances, have been isolated. It is proposed to place on record a miscellany of these observations on some future occasion. The present case seemed of sufficient interest to warrant a separate record.

Corydalis ochotensis Turcz. is a native of the vicinity bordering the Sea of Okotsk in Eastern Siberia. It appears to be an obligate biennial, producing during the first year of its growth a fleshy sub-tuberous tap-root, 12 to 16 cm. in length, which during the second year of growth to maturity sends out numerous fibrous roots. In this process the original tap-root itself shrinks to a somewhat insignificant primary root. The main stem as well as the branches and petioles are irregularly tetragonal in cross section. The ultimate segments of the compound leaves are almost circular in outline. The seed pod is flat and curved. At maturity it is under stress and discharges the black seeds with considerable force when disturbed. The entire plant is glaucous green and the much branched and reclining stem may attain a length of 1 to 1.5 metres (5).

The material for the present work was grown in a local garden from seed obtained through the courtesy of Mr. John Adams, Botanist at the Central Experimental Farm, Ottawa. After the first year of growth the plants were collected and the leaves severed from the roots. The latter after washing and drying were ground to a coarse powder. Following the usual procedure, the material was extracted in a Soxhlet apparatus with methanol. During the course of this extraction a substance crystallized from the hot extract in large stout crystals which had the appearance and taste of sucrose. After cooling, filtering and washing thoroughly with methanol the yield of product based on the weight of air-dried roots was 10%.

It soon became evident that this substance was not sucrose, and in fact it was found to contain nitrogen. This observation together with its strong sweet taste suggested an amino-acid, and the test with triketo-hydrindene hydrate (ninhydrin) gave an intense blue color even in very dilute solution. Kjeldahl analysis showed 15.4% nitrogen and a van Slyke amino-nitrogen determination gave 9.2%. The well crystallized copper salt contained 14.9% copper and 13.1% nitrogen. These figures indicate a copper to nitrogen ratio of 1 to 4 and an amino-nitrogen to total nitrogen ratio of 1 to 2. Further, on the basis of a mono-basic acid, the molecular weight is 172 or 174 corresponding to $C_7H_{12}O_3N_2$ or $C_7H_{14}O_3N_2$ respectively. Such a substance could be a dipeptide but none appeared to have been described which might be regarded as identical with it.

An attempt was therefore made to hydrolyze it with dilute sulphuric acid in order to identify the hydrolytic fragments. Unexpectedly, however, acetic acid proved to be one of the hydrolytic products. On the basis therefore of the $C_7H_{14}O_3N_2$ formula the second fragment must be $C_5H_{12}O_2N_2$, that is, ornithine or an isomeric diamino-valeric acid. Removal of the sulphuric acid from the hydrolyzed solution by means of baryta yielded a strongly basic solution of the amino-acid. This readily dissolved in methanol and yielded a picrate melting at 207° C.* Riesser (6) gives 198–199° (?corr.) for the melting point of *d*-ornithine picrate. An authentic specimen of *d*-ornithine picrate which melted at 207° C. was kindly supplied by Dr. H. B. Vickery, Connecticut Agricultural Experiment Station, New Haven, Conn., and in admixture there was no depression in the melting point. The substance therefore is mono-acetyl-*d*-ornithine, $CH_3 . CO . NH . CH_2 . CH_2 . CH_2 . CH(NH_2) . CO_2H$. The alternative position for the acetyl group is excluded because of the positive ninhydrin reaction and presumably also because of the sweet taste of the substance. The positive rotation of 13.1° clearly relates this amino-acid to natural *d*-arginine and *d*-ornithine.

The author is not familiar with an analogous case in the domain of phytochemistry. There does not appear to be any good reason why ornithine should be the chief nitrogen requirement of this particular plant and, further, why an acyl derivative should be the choice. Acyl and aroyl derivatives of amino-acids are animal catabolites and serve to eliminate injurious acids from the animal body. Dibenzoyl-ornithine (ornithuric acid) and hippuric acid play this role in birds and mammals respectively for the elimination of benzoic acid. In the case of *C. ochotensis*, however, acetyl-ornithine can be regarded only as an intermediate metabolic product serving as a nitrogen reservoir.

It may be added that ornithine plays an important role in the well known mechanism which Robinson (7) has advanced to account for the phytosynthesis of alkaloids from amino-acids, and it may be significant that this particular plant does elaborate a number of alkaloids. Many workers have

* *Melting points are corrected.*

investigated the non-protein, non-alkaloidal nitrogenous substances in plants, but the author is not aware of such an investigation of a plant known to contain alkaloids except perhaps tobacco. Free amino-acids are of fairly common occurrence, but they appear to be used as a vehicle for translocating nitrogen and not as nitrogen reservoirs. The latter role is traditionally played by proteins, and the amides asparagine and glutamine.

Dr. Vickery, to whom this paper has been submitted, has kindly prepared some comments of which the following is a summary.

"The general behaviour of the plant makes it appear possible that acetyl-ornithine is the substance utilized to care for an accumulation of a highly basic constituent which, if present in the free form, might become toxic through its influence on the pH. This would be closely analogous to the manner in which the beet root cares for an excessive quantity of ammonia by converting it into glutamine.

"In pursuit of this speculation the metabolism of the plant may involve an accumulation of arginine and the co-presence of arginase, so that the tissue may contain not only ornithine but urea as well. It would seem logical therefore to look for evidence of the presence of arginase and of urease and urea.

"Should urease be present, then the root should store not only the ornithine but also either asparagine or glutamine since the ammonia would be detoxicated by the synthesis of one of these amides.

"From this point of view one would perhaps question the implication that acetyl-ornithine is the chief nitrogen requirement of this particular plant. . . . ."

The questions here raised can be decided only by further work, and it is hoped that when more material becomes available some of the moot points may be clarified.

Experimental

Mono-acetyl-ornithine

The crude acetyl-ornithine, obtained as described above, was dissolved in water and the turbid solution filtered with the aid of infusorial earth and charcoal. A small amount of colloidal matter made this filtration extremely difficult and tedious. Even the filtrate retained a turbidity which could not be completely removed by further filtration. The colorless solution was evaporated *in vacuo* to incipient crystallization and then treated with hot methanol. The finely crystalline material was filtered off and washed with cold methanol. Further purification, and the elimination of all but a trace of ash, was accomplished by recrystallizing from methanol in a Soxhlet apparatus, the chief objection here being the vigorous bumping which occurred when some of the substance had crystallized in the extract. As thus obtained, mono-acetyl-ornithine consisted of colorless fine plates which melt with decomposition at 266° C. $[\alpha]_D^{24} = +13.1°[c = 4$ in water]. Calcd. for $C_7H_{14}O_3N_2$; C, 48.28; H, 8.05; N, 16.1; amino-N, 8.1%. Found: C, 48.30; H, 7.85; N, 15.4; Amino-N, 9.2%.

Acetyl-ornithine gives a precipitate with phosphotungstic acid, but not with mercuric chloride; picric acid or flavianic acid.

The copper salt was prepared by boiling a suspension of copper carbonate in an aqueous solution of the acid. It crystallized from the concentrated solution while still hot and was recrystallized from a large volume of hot water. Pale blue plates were thus obtained. The substance is only slightly soluble in cold water. Calcd. for $C_{14}H_{26}O_6N_4Cu, H_2O$; Cu, 14.9; N, 13.1%. Found: Cu, 14.9; N, 13.1%.

Hydrolysis

Three grams of the amino-acid was dissolved in 25 cc. of water to which 5 gm. of concentrated sulphuric acid had been added. The solution was heated to boiling and then left on a steam bath overnight in a loosely stoppered flask. A pronounced odor of acetic acid had developed. The solution was evaporated to a small volume *in vacuo* and the acetic acid identified as follows: The distillate was neutralized with a measured amount of potassium hydroxide and evaporated to dryness on a steam bath. The saline residue was dissolved in a small volume of water and heated for an hour on the steam bath with an ethanolic solution of xenacyl bromide containing 75% of the calculated amount. On cooling, the xenacyl acetate crystallized in colorless flat plates melting at 111° C. Drake and Bronitsky record the same melting point (1).

The residue from which the acetic acid had been distilled was diluted with water and again evaporated *in vacuo*. The aqueous solution of the residual syrup was then quantitatively freed of sulphuric acid by means of barium hydroxide, and the colorless filtrate evaporated to dryness *in vacuo*. This was dissolved in methanol and a small amount of insoluble residue removed by filtration. A portion of the filtrate was treated with a methanolic solution of picric acid. On evaporation to a small volume, ornithine picrate crystallized in pale-orange fine prisms sparingly soluble in methanol. It melted at 207° C. after one recrystallization from hot water, and in admixture with an authentic specimen of *d*-ornithine picrate which melted at the same temperature there was no depression in melting point.

Dibenzoyl-ornithine

A mixture of ornithine and its carbonate obtained from the acetyl-compound was benzoylated with benzoyl chloride in alkaline solution by Fischer's method. The recrystallized dibenzoyl-ornithine melted at 189° C. Fischer (2) gives the melting point as 187–188° C. corr. (184° C. uncorr.). Jaffé (3, 4) gives 182° C., presumably uncorrected.

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THE INFLUENCE OF PENETRATION IN THE ALKALINE DELIGNIFICATION OF WOOD[1]

BY GERARD L. LAROCQUE[2] AND O. MAASS[3]

Abstract

The effect of various factors that might possibly influence the penetration of soda liquor into spruce wood has been examined. It was found that the rate of delignification was the same irrespective of the size of the sample, from a wood-meal of 0.005 mm. particle size up to a limiting chip thickness of about 10 mm. The density of the wood had no influence on the delignification other than that which would be expected from the higher original lignin content of the more dense wood. The presence of moisture in the chips was without result other than that of diluting the liquor, and the addition of wetting agents for facilitating the penetration rate was without significant effect.

Introduction

The digestion of wood in aqueous alkaline solution has long been an important process for the commercial preparation of cellulose pulp. Investigations of the mechanism of this process have been made from time to time, but no satisfactory explanation has yet been given for the complete reaction. From the chemical point of view, the process consists essentially in the formation of a water-soluble alkali-lignin compound, the cellulose being only slightly affected. The exact physico-chemical nature of this process is unknown. The manner in which such variables as concentration of the alkali, temperature, rate of penetration of the liquor, size and moisture content of the chip, etc., affect the rate of the delignification process, has never been the subject of an exhaustive survey in which all these factors were considered at the same time.

Macklin and Maass (3) developed a suitable experimental procedure for carrying out cooking experiments on a small scale under closely controlled and reproducible conditions, and they paid special attention to the delignification of spruce wood with sodium hydroxide solutions of high concentration. Their experimental technique was adopted in the present investigation, which was primarily concerned with an examination of those purely physical factors, such as size and shape of the wood chip, method of liquor penetration into the wood during the cooking process, density and moisture content of the wood, etc., that might affect the delignification process by influencing the rate of penetration of the active chemicals into the wood.

The role played by the alkali, and the probable kinetics of the process will be considered in a subsequent paper. A further paper will discuss some observations on the quality and strength of pulps prepared under special experimental conditions. This may be of interest in the commercial application of the alkaline pulping process.

Experimental Procedure

The method employed consisted in carrying out small-scale pulping experiments with specially prepared wood chips in digesters of 80 to 200 cc. capacity under closely controlled conditions in regard to time, temperature, alkali concentration and pressure. The experimental conditions could then be varied one at a time and the resulting pulp examined for yield and carbohydrate, lignin content and quality, in accordance with a standardized procedure.

This technique has been described in detail by Macklin and, Maass (3) and is briefly as follows: In those experiments requiring a continuous flow of liquor of constant composition through the digester during the cooking process, an Allegheny metal cell of 80 cc. capacity was charged with 10 gm. of air-dry wood chips 2 by 10 by 20 mm. The cell was thoroughly evacuated at a pressure of about 2 cm. of mercury. The cooking liquor was then introduced under a pressure of 125 lb. per sq. in. (gauge). It flowed through the cell at the rate of 5 cc. per min. during the entire period of digestion. In this manner, the liquor concentration in the cell remained constant during the delignification reaction. The cell was heated and electrically controlled at 160° C. in an oil bath. The wood used was naturally seasoned black spruce, the chips being cut along the grain. Their density and original lignin content is indicated in each set of experimental results. This procedure is called "forced penetration" of the liquor, with pre-evacuation and liquor flow. An alternative procedure was "natural penetration" of the liquor, in which the liquor was added to the chips at atmospheric pressure and without any pre-evacuation of the wood. The pressure within the chip then built up slowly as the temperature was raised, and penetration of the cooking reagent into the wood was hindered by the presence of the air in the wood.

At the end of the digestion period, which was usually of three hours duration, the reaction was stopped by plunging the cell into cold water.

The cooked chips were broken up into single fibres by a motor-driven, propeller type of disintegrator, and thoroughly washed. Approximately 1.2 gm. (air-dry basis) of the wet pulp was made into a hand sheet. After it had been conditioned for two hours at 65% relative humidity and 70° F., the sheet was tested for bursting strength on a motor-driven Mullen tester, according to the standard procedure set by the Technical Section of the British Paper Makers Association (5). The bursting values obtained were converted into per cent Mullen on the basis of 25 by 40 in. 500 sheet ream by multiplying the mean burst value observed by the factor 2.82 and dividing by the air-dry weight (in grams) of the sheet.

The remainder of the pulp, and the test sheet were then dried to constant weight in an oven at 105° C., and the yield of pulp was expressed as a percentage of the original bone-dry wood. Half-gram samples of the pulp were then analyzed for lignin content by the formaldehyde-sulphuric acid method, as described by Macklin and Maass (3). The lignin is expressed as a percentage of the original bone-dry wood.

Experimental Results and Discussion

A number of experimental conditions that might be capable of influencing the penetration of the alkaline pulping liquor into the wood chip have been investigated separately. Since these conditions are largely unrelated to one another, except in so far as they may simultaneously affect the process, it was considered advisable to present and discuss these factors under a number of separate headings. In each set of experimental results, the procedure used was that described above, unless otherwise modified as indicated. Detailed observations have been omitted, and the results have been tabulated to an extent considered compatible with clarity. A short discussion follows each set of experimental results.

Previous investigators of the soda process have used wood chips that were only approximately uniform in size in order to obtain comparable and reproducible results. In the present investigation however, one standard size of chip, 20 by 10 by 2 mm. was used throughout in order to compare the influence of different variable factors under similar experimental conditions. Nevertheless, it was deemed important to determine at the beginning of the investigation the limiting size of chip at which diffusion processes began to seriously hinder the rate of delignification, and second, whether the rate of delignification of very fine wood-meal was higher than that of chips of standard size.

Wood-meal

In this series of experiments, wood-meal of 250-300 mesh screen, which had been extracted with water, alcohol-benzene and methyl alcohol, was used. It therefore contained only cellulose, lignin and hemicellulose. The digestion was carried out with natural penetration of the liquor, in cast-iron bombs of 200 cc. capacity containing 165 cc. of 2.0 M sodium hydroxide at 160° C. The lignin contents of the resulting pulps and the values obtained with chips of standard size are reported in Table I.

TABLE I

DELIGNIFICATION OF WOOD-MEAL

Time, hr.		0.0	1.08	1.75	3.0
Lignin in pulp, %	Wood-meal	30.1	21.0	15.2	7.8
	Wood chips	30.2	21.5	14.6	7.6

The results were confirmed with wood-meal and chips prepared from a sample of a different density. In every case, identical residual lignin values were obtained in the pulp whether the wood used was in a finely comminuted state or chips 20 by 10 by 2 mm.

It is surprising that the extent of the delignification at different time intervals during the process should be no greater with a finely ground 250–300 mesh material (particle size of about 0.005 mm. in diameter) than for chips 2 mm. in thickness. This indicates, primarily, that the diffusion of the alkali into, and of the reaction products through, the cellular passages of a chip of this size is not a factor that affects the rate of reaction; and secondly, that the lignin present in a finely ground wood-meal having a particle size of 0.005 mm. does not dissolve more readily than the lignin that is embedded in the cellulose in the solid wood chip. All the lignin is equally accessible to the reagent, and therefore there is in effect a homogeneous type of chemical reaction.

The Influence of Chip Size

The next step was to determine the maximum chip size, above which the wood structure hindered the penetration of the alkali and the outward diffusion of the reaction products sufficiently to affect the rate of delignification. Since Lusby and Maass (2) had shown that diffusion of sodium hydroxide in aqueous solution took place with equal rapidity in the three structural directions of wood chips, it was decided to use cubical wood specimens of 10, 15 and 20 mm. edge, in this part of the investigation.

Two different experimental procedures were used. In the first, termed "forced penetration", the chips in the cell were evacuated, and liquor was then introduced under 125 lb. pressure (gauge). The wood was impregnated with liquor at the very start of the cook, so that penetration of the alkali could then take place freely, by processes of diffusion and unhindered by the presence of air.

In the second procedure, called "natural penetration", there was neither evacuation nor application of pressure. The chips were simply covered with liquor in a cast-iron bomb. With rise in temperature, penetration took place slowly under the vapor pressure of liquid, and retarded by the presence of the air phase in the chip.

With these two different methods of procedure, cooks were carried out with black spruce wood of density 0.43 and lignin content 30.9%, at 160° C. for various lengths of time with 2.0 M sodium hydroxide. The residual lignin content of the pulped chips is given in Table II.

In the case of the three pulp samples marked with an asterisk, a considerable portion of the yield, namely 10% of the 15 mm. chips and 29 and 42% of the 20 mm. chips consisted of hard uncooked wood with a lignin content of 30 to 36%. On the other hand, no hard uncooked centres were observed in the chips that had been cooked with forced penetration of the liquor, although of course shives were present till the third hour.

TABLE II
Chip size and delignification

Time, hr.	Dimensions of chips, mm.			
	2 by 10 by 20	10 by 10 by 10	15 by 15 by 15	20 by 20 by 20
	Lignin in pulp, %			
"Forced" liquor penetration				
0.00	30.9	30.9	30.9	
1.00	21.0	22.8	27.0	Only shives
2.00	12.5	12.5	17.5	Few shives
3.00	7.8	8.5	11.5	Well cooked
"Natural" liquor penetration				
0.00	30.9	30.9	30.9	30.9
1.75	—	—	—	20.1*
3.00	6.3	8.7	11.1*	12.2*

This gives some indication of the extent to which the presence of air can retard the cooking process by interfering with the entry of the cooking liquor into the interior of the chip.

In both procedures the chips kept their shape throughout the cook, and the progress of the cooking action could be followed by cutting the chip in half and examining it in cross section. Cooking was observed to take place in three separate stages from the exterior of the chip inwards, and could easily be followed by the color changes taking place.

In the first stage, following the penetration of the liquor, there was a slight softening of the chip, and the wood was still light in color. Some of the pentosan material having been dissolved, the lignin content accordingly rose above that normally present in wood. Such a chip would not be mechanically disintegrated into pulp fibres. This condition still prevailed in the interior of the 15 mm. and 20 mm. chips that had been cooked for three hours without pre-evacuation or forced liquor penetration, but was absent in the other chips.

In the second stage, the outer portions of the chip became softer and darker. The distinct boundary line separating this softer portion from the hard yellow centre moved slowly inwards until the chip was uniform in appearance and texture throughout. The chip could then be completely disintegrated into pulp and fine shives, but could not be entirely broken up into individual fibres. This pulp made a fairly good sheet having a strength value of from 60 to 80 M.B.R. The yield would be 55% or more, and the lignin content about 18% on a pulp basis.

In the third stage of the pulping process, the chip became much softer and lighter in color. This corresponded to the removal of the remaining lignin from the middle lamellae, and the chips could be completely disintegrated into individual fibres. At this stage, pulp yields fell below 50%, and a point

is reached where, in commercial operation, the decrease in lignin content no longer compensates for the simultaneous loss of cellulose, and it is more profitable to stop the digestion at this stage and remove the remaining lignin by a bleaching operation.

In conclusion, it may be stated that the rate of delignification is the same irrespective of the size of the chip, from 250 mesh particles up to cubical chips of 10 mm. edge. For chips of greater thickness than 10 mm. but less than 20 mm., the reaction is greatly retarded by the resistance to penetration offered by the air-phase in the chip. In the absence of this air, the rate remains substantially unaffected. For chips that are 20 mm. and more in thickness, diffusion processes begin to retard the reaction rate even when the air in the chips has been removed.

The slower delignification rate observed with the chips of larger size may be attributed to two causes. Either the alkali is being used up more rapidly in the interior of the chip than it can be supplied by diffusion, or else the out-ward diffusion of the reaction products may have been retarded sufficiently to accumulate in the interior of the chip, and interfere at the reaction inter-face. Either phenomenon would cause the observed decrease in reaction rate, and will be discussed in greater detail in a subsequent paper dealing with the mechanism of the reaction.

For the present, the effect of penetration in subsequent work will be eliminated by the use of a standard wood chip 2 mm. thick, 10 mm. wide and 20 mm. long in the fibre direction.

Wood Density

The spruce wood used in commercial pulping practice is found to vary considerably in density. The average sample has a bone-dry specific gravity of about 0.45, but wood specimens of density 0.35 or 0.55 are quite common. Such variations in the density of the wood structure might be expected to affect the liquor penetration. Furthermore, a higher lignin content is generally associated with the denser wood. It was interesting therefore to determine how the high density wood differed from the low density wood in behavior on delignification. Three different experimental procedures were used, in order that the conclusions might be general in their application.

In Series I, a cell of 80 cc. capacity was used with 10.0 gm. of 20 by 10 by 4 mm. chips, with pre-evacuation and forced penetration of the liquor, but without liquor flow during the course of the digestion. In Series II, the conditions were the same except that fresh liquor flowed continuously through the cooking cell during the reaction. In the third series, bombs of 200 cc. capacity were used, with natural penetration of the liquor. The wood in every case was cooked for three hours at 160° C. in accordance with the standard procedure.

The resulting yields of lignin and carbohydrate, expressed as a percentage of the original bone-dry wood are given in Table III, together with the density of the wood and the strength of the resulting pulp.

It is to be noticed that: (i) The wood of higher density gave a pulp of higher lignin content, but only to the extent which would be expected from the higher lignin content originally associated with the wood of higher density. (ii) Higher yields of carbohydrate were always obtained from the woods of lower density, in accordance with their lower lignin contents. (iii) There is a marked decrease in paper strength with increase in wood density, which is to be ascribed to the shorter fibre length of the high density wood. (iv) These conclusions were found to hold, independently of the particular cooking procedure followed.

TABLE III
THE EFFECT OF WOOD DENSITY

Series	Wood density	Lignin, %	Carbo-hydrate, %	Strength, % Mullen
I	0.34	3.8	45.1	114
	0.54	5.6	42.6	80
II	0.41	3.7	42.4	144
	0.51	4.6	39.8	116
III	0.35	2.8	41.0	113
	0.45	3.4	40.5	97

Moisture Content

In commercial wood-pulping practice, wide variations occur in the moisture content of the wood. The wood may have been stream-driven and contain 40% of water, or it may have been kept in storage for one or more years, and have a moisture content as low as 6%. This is a variable that might influence the reaction, since the imbibition of moisture is accompanied by a swelling of the wood and a constriction of the passages available for liquor penetration. It was therefore desirable to determine what effect the initial water content of the wood had upon the cooking results.

The standard size of chip, 20 by 10 by 2 mm. was used, with 2.0 M sodium hydroxide liquor, and cooked for three hours at 160° C. In the first set of experiments, a bomb of 80 cc. capacity was employed containing 10 gm. of wood and 18 gm. of water. No correction was made to the liquor concentration for the dilution caused by the water content of the chips. In the second set, bombs of 200 cc. capacity were used containing 165 cc. of 2.0 M liquor, the liquor concentration being corrected for the decrease in concentration caused by the water present in the chips.

TABLE IV
EFFECT OF MOISTURE CONTENT UPON DELIGNIFICATION

Series	Moisture, %	Lignin, %	Carbo-hydrate, %	Strength, % Mullen
I	6.6	6.8	47.0	110
	180·0	3.3	45.3	113
II	6 8	4.5	44.3	107
	86·0	3.9	43.6	to
	100·0	3.6	46.9	
	180·0	3.9	44.8	111

It is seen that if the liquor is corrected for the decrease in concentration brought about by the water content of the chips, then the presence of moisture has no effect upon either the extent of delignification or the strength of the pulp. This holds only for alkali cooking; deMontigny (1) has shown that in sulphite cooking an increase in moisture content from 18 to 84% brings about an increase in lignin content from 4 to 15% and a decrease in paper strength from 260 to 125% Mullen. The reason for this difference in behavior is that, in sulphite cooking, the liquor has not as great an initial solvent action upon the incrusting materials as has the sodium hydroxide liquor. Consequently, liquor penetration has to take place almost entirely from tracheid to tracheid along the fibre direction of the wood, in which case, as Sutherland (4) has shown, the forced penetration is hindered by a "Jamin tube" effect. Drops of liquid and bubbles of gas alternate in the tracheid of wood of a high moisture content. As a result, such a system transmits less pressure than it receives. The forced penetration of the sulphite liquor into the chip is therefore retarded, and pulps of high lignin content and low strength are obtained.

On the other hand, Lusby (2) has shown that, in soda cooking, penetration takes place with equal ease in the three structural directions of the wood, owing to solvent action in the initial stages of the penetration process. Consequently, the presence of moisture up to saturation presents no difficulty to liquor penetration by diffusion. The only noticeable effect is the dilution of the liquor resulting from the higher water-content of the wood.

The observed variations in carbohydrate yield may be due to errors inherent in the method, because with such a heterogeneous substance as wood the yield values are subject to erratic and inexplicable variations, so that only the mean value obtained from several experiments carried out under identical conditions can be taken as an indication of how the yield was influenced by a certain treatment.

Wetting Agents to Assist Penetration

It has been previously shown that, for chips below a certain size, resistance to penetration is not sufficient to influence the rate of the delignification reaction. However, it might be that in all these cases a slower submicroscopic penetration of the alkali ions into the fine gel structure of the wood and lignin is taking place. This submicroscopic penetration might be the factor limiting the reaction rate. It was thought, therefore, that if traces of the sulphonated fatty alcohols were added to the cooking liquor, they would lower the surface tension of the advancing liquor phase and might cause a more rapid and thorough impregnation of the ultimate wood substance, and thus favorably influence the properties of the pulp. A number of such wetting agents, of the general formula $R \cdot OSO_3 \cdot Na$ were therefore added in small amounts to the cooking liquor. Compounds *A* and *B* are the sodium salts of the sulphonated lauryl and oleyl alcohols. *C* is a similar compound but of higher molecular weight. *D* is a sulphonated naphthalene derivative.

The wetting agents were added to the extent of 0.2% to 165 cc. of 2 *M* sodium hydroxide liquor and 10 gm. of wood chips of the standard size. The chips were cooked at 160° C. for three hours, and without any preliminary forced penetration of the liquor into the chips. In Table V is given the percentage yield of pulp and the bursting strength of the paper made therefrom which is a good measure of the pulp quality.

TABLE V

THE INFLUENCE OF WETTING AGENTS ON PENETRATION

Wetting agent	None	A	B	C	D	D (0.04%)
Pulp yield, %	44.2	43.7	43.7	41.7	43.3	43.2
Pulp strength, % Mullen	115	88	106	92	108	108

The effects observed were small, however, and generally unfavorable. It would seem therefore that sulphonated fatty alcohols added to the alkali liquor in small amounts do not markedly affect the results of the soda process by facilitating the liquor penetration. The effect upon paper strength is small and generally unfavorable.

Conclusions

The salient facts that arise from a consideration of the influence of liquor penetration in the alkaline delignification of wood are the following: In general, the wood structure offers but little hindrance to the delignification reaction for chips up to 10 mm. in thickness, even with completely air-filled wood. A very finely ground wood-meal gave no increased rate of reaction. Moreover, the presence of moisture in the wood to the extent of fibre saturation was without pronounced influence upon the reaction rate, and the delignification was not sensibly different in wood specimens of high density. No advantage furthermore was to be gained through the addition of wetting agents to the cooking liquor in order to facilitate the penetration process.

In general, therefore, it can be stated that penetration of the soda liquor into the gross structure of the wood substance, and the outward diffusion of the reaction products, are not the determining factors in fixing the velocity of the rate of delignification.

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EQUILIBRIA IN LIQUID SYSTEMS CONTAINING FURFURAL[1]

By B. A. Lloyd[2], S. O. Thompson[3] and J. B. Ferguson[4]

Abstract

The solubility curves and tie-lines at 25° C. were determined for the systems acetone-water-furfural, water-furfural-ethyl acetate and water-furfural-isoamyl acetate.

Introduction

The mutual solubilities of water and furfural were studied by Rothmund (13), Mains (9), and Evans and Aylesworth (3). Qualitative information concerning more complicated systems containing furfural has been given by Jänecke (8) and especially by Hammer (5). There is little, if any, quantitative information on such systems in the literature. An extended study of the more common solvents is not to be expected, but a limited amount of quantitative information on each solvent should be available.

Materials and Procedure

The furfural was purified by steam and by vacuum distillation. It boiled at 161.7° C. $\pm$ 0.1°. It was kept in dark colored bottles (9, 12) and no material was used that was more than a week old (4). The purity of the furfural was checked by the redetermination of the solubilities for the system water-furfural, using the procedure of Mueller (11). The results so obtained agreed with those of Evans and Aylesworth. A badly discolored sample was used to test the effect of the impurities on the solubility. The saturated solutions were not particularly sensitive to these impurities; for example, the consolute temperature was raised from 118 to 120° C. in one experiment.

C.p. acetone was dried and redistilled; c.p. isoamyl acetate was fractioned by distillation and the fraction that was taken boiled at 141.6° C. $\pm$ 0.1° at 754 mm. of mercury. C.p. ethyl acetate was washed with water and distilled. The fraction that was used had a density $D^{20}_4 = 0.9006$; Wade and Merriman's value (14) was $D^{20}_4 = 0.90056$.

The solubility curves at 25° C. were determined by titration. The container was a Pyrex glass tube, 12 mm. bore and 60 mm. long, sealed at both ends. A tube of 3 mm. bore, through which the reagents were introduced, was sealed to the side of the Pyrex tube. A known two-component sample was placed in the container and the latter was put in a thermostat, kept constant at 25° C. $\pm$ 0.1°, so that the side tube projected above the bath liquid. The third component was introduced by means of a small weight burette equipped with a long fine delivery tip. The side tube was stoppered when not in use. Stirring was effected by a suitable rotation of the container in a plane that differed slightly from the horizontal. This caused the gas bubble, present in the large tube, to move from one end of it to the other and thus to stir the liquid.

The tie-lines were obtained from the weights of the two phases in a sample of known composition by the method of Miller and McPherson (10), or from these weights and the furfural content of the furfural-rich phase. Furfural was determined by the colorimetric method of Fleury and Poriot (15, p. 419). The known sample was placed in a glass vessel somewhat similar to an Ostwald pycnometer, but with longer capillary leads that projected above the bath liquid. After shaking, the phases were allowed to separate at constant temperature. The lower phase was removed through the lower capillary without exposing the main part of the container to the air. The weights of the separated phases were checked against the total weight of the sample.

The plait point for the system acetone-water-furfural was approached experimentally, and checked by the extrapolation of the line through the mid-points of the tie-lines.

Results

The binary solubilities for furfural-water had not been determined at 25° C. For water in furfural the value that was obtained by the interpolation of the results of Mains was satisfactory, but the corresponding value for furfural in water did not agree with the writers' results for the ternary systems, and Thompson's value was substituted for it. The mutual solubilities of water and isoamyl acetate were so small that Bancroft's value (1) at 20° C. was assumed to be satisfactory for 25° C. The mutual solubilities of ethyl acetate and water are given in I.C.T. (7, p. 388), and these were confirmed by the writers.

The binodal curve, the tie-lines and the plait point for the system acetone-water-furfural are shown graphically in Fig. 1. Owing to the large areas of
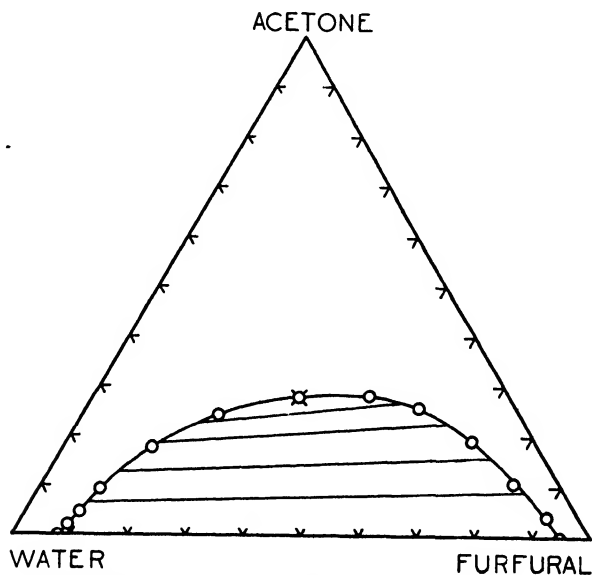
FIG. 1. *The binodal curve, the tie lines and the plait point for the system acetone-water-furfural at 25° C.*

immiscibility on the phase diagrams for the other systems, these diagrams are not given. The numerical results are listed in Tables I, II and III.

TABLE I

THE SYSTEM ACETONE-WATER-FURFURAL AT 25° C.

Weight percentage—$a + b + c = 100$

The binodal curve

Acetone (a)	Furfural (c)	Acetone (a)	Furfural (c)
0.0	7.7	0.0	94.7
2.2	8.5	4.0	90.3
4.7	9.3	10.6	81.6
9.4	10.5	19.3	70.1
17.9	15.1	25.8	57.7
24.1	23.4	28.0	47.8
	Plait point	27.4	35.8

The tie-lines

	The furfural content			
Phase I	21.0	16.0	12.2	10.0
Phase II	53.5	64.0	74.5	84.0

TABLE II

THE SYSTEM WATER-FURFURAL-ISOAMYL ACETATE AT 25° C.

Weight percentage—$a + b + c = 100$

The water-rich phase		The water-poor phase	
Furfural (b)	Isoamyl acetate (c)	Furfural (b)	Water (a)
0.0	0.2	0.0	1.2
1.8	0.5	9.7	1.1
3.8	0.4	19.7	1.6
5.8	1.2	29.5	1.8
7.3	1.9	39.9	2.1
7.7	0.0	43.2	2.2
		48.2	2.4
		53.5	2.9
		58.4	2.6
		78.4	3.6
		88.8	4.6
		94.7	5.3

The tie-lines

	Phase I		Phase II	
The furfural content	2.0	16.0	4.2	36.0

TABLE III

THE SYSTEM WATER-FURFURAL-ETHYL ACETATE AT 25° C.

Weight percentage—$a + b + c = 100$

The water-rich phase		The water-poor phase	
Furfural (b)	Ethyl acetate (c)	Furfural (b)	Water (a)
0·0	7.56	0·0	3.24
1.7	6.6	3.3	3.5
3.9	4.9	6.9	3.4
5.3	3.2	15.8	4.3
6.5	2.4	21.9	4.2
6.8	1.9	33.3	4.1
7.4	0.6	51.4	4.4
7.7	0·0	60.7	4.8
		71.9	4.6
		74.7	4.9
		86.3	5.1
		94.7	5.3

The tie-lines

	The furfural content		
Phase I	3.8	5.0	6.7
Phase II	31.9	70.5	90.1

Discussion

In the system water-acetone the partial pressures at 25° C. (2) show a large positive deviation from Raoult's law, and one might infer that the system is not far removed from systems that show liquid immiscibility. For this reason, a greater area of immiscibility was expected than is shown in Fig. 1. The tie-lines for this system do not agree closely with the empirical equation of Hand (6),

$$\frac{a}{b + kc} = \frac{a'}{b' + kc'}$$

but there can be no doubt that this equation offers a practical solution of the problem of the interpolation between determined tie-lines for many cases of dineric distribution.

The water-rich and the water-poor series of saturated solutions in the systems that contain ethyl acetate or isoamyl acetate should each lie on curves that intersect. When the results given in Tables II and III are plotted, definite breaks are evident for the water-rich series. There is an indication of a break on the water-poor isoamyl acetate curve at 45% of this component, but there is none on the corresponding ethyl acetate curve, although the tie-lines indicate there should be one at approximately 90% furfural. Since the solutions of furfural in ethyl acetate and in isoamyl acetate do not dissolve more water than do the pure solvents, these solutions would not be expected to dissolve water-soluble materials to a much greater degree, and in this respect should be as efficient differential solvents.

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THE BASE-EXCHANGING PROPERTIES OF SYNTHETIC ALUMINO-SILICATE MATERIALS. II.[1]

By J. R. Patton[2] and J. B. Ferguson[3]

Abstract

The base-exchanges $Ca^{++} \rightleftarrows Na^+$ and $Ba^{++} \rightleftarrows Na^+$ have been studied with Doucil and various salt solutions. The calcium or barium content of the gel increased as the concentration of the solution decreased. With the more concentrated solutions, the calcium content of the gel increased with increasing temperature; at the same temperature, the calcium content was greater when calcium Doucil replaced sodium Doucil as the initial gel material. Solutions of calcium nitrate and of calcium acetate gave similar results, but these were higher than those obtained with calcium chloride solutions.

The exchange reaction is chiefly determined by the relative cationic content of the gel and of the solution, but the actual amount of exchange taking place in a given case is greatly dependent upon the available capacity, which is in turn dependent upon those factors that affect the penetration of the gel. The effects of temperature, of concentration, of the kind of anion and of the kind of gel are thought to be more closely related to the penetration phenomena than to the exchange reaction proper. Although the direction of the effect of concentration is indicated by the equation of Rothmund and Kornfeld, the results are not in quantitative agreement with this equation. The equation $\dfrac{P}{E'_1} = a + bP$ is useful for the interpolation of curves obtained at constant anionic normality, especially if the solutions are dilute.

Introduction

The base-exchange reaction with artificial alumino-silicate gels usually proceeds rapidly at first, and then so slowly that a state of equilibrium is commonly assumed to have been reached at this stage. The steady states probably represent a close approximation to states of equilibrium involving those portions of the solid in which a rapid diffusion is possible. This diffusion is dependent upon various factors, and it is not easy to determine the amount of the solid that is reacting, or, in other words, the actual capacity. Many of the published base-exchange curves are a record of the above-mentioned steady states, and their actual significance needs further elucidation.

The earlier paper (1) dealt with the base-exchanges $Ag^+ \rightleftarrows Na^+$ and $Cu^{++} \rightleftarrows Na^+$. The work has now been extended to include the reactions $Ca^{++} \rightleftarrows Na^+$ and $Ba^{++} \rightleftarrows Na^+$ with Doucil as the gel material.

Experimental

The Doucil was selected from a large sample of commercial material. The analysis by Patton is: Na_2O, 10.29; Al_2O_3, 14.86; SiO_2, 53.08%. Water was not determined. The corresponding weight percentages given by Musgrave for his Doucil were: 10.26; 14.65 and 52.35.

The samples of gel material were ground to pass a 100 mesh screen and the portions that were retained on a 200 mesh screen were used. A weighed amount of this material was placed in a glass-stoppered bottle to which was

added a known amount of a known salt solution. The selection of the proper amounts was simplified by the use of the linear relation employed in Fig. 2 when the approximate position of the curve was known. The bottle was placed in a thermostat and shaken for 1.5 hr. Trial experiments showed that a steady state was reached within an hour, and that this state was not appreciably changed at the end of 12 hr. if calcium nitrate solutions were used. The bottle was removed from the bath and the contents filtered and analyzed. Since the amount and the composition of the gel and of the solution initially taken were known, the amount of one base in the final solution sufficed for the calculation of the composition of the final solution and of the amount of the exchanged base in one unit of the final gel. The change in the composition of the solution was assumed to be caused by an exchange reaction with the gel.
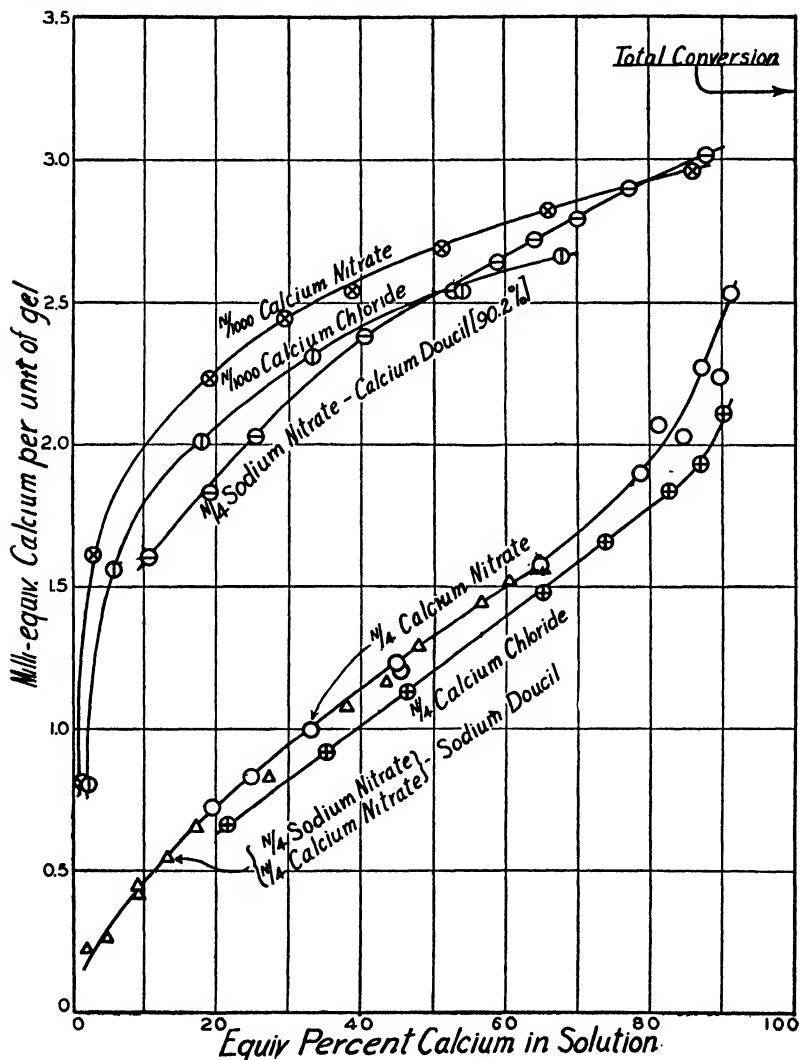
FIG. 1.   *The Doucil base-exchange curves for the* $Ca^{++}\rightleftharpoons Na^+$ *reaction at 21° C.*

Calcium was determined as the oxalate, and barium as the sulphate. Sodium Doucil was decomposed with aqua regia. Calcium Doucil was fused in a nickel bomb with sucrose and sodium peroxide. When decomposed, the gels were analyzed by the standard methods for rock analysis. The very dilute solutions were concentrated on a water bath, and blank determinations were made in all cases. In the experiments with $N/1000$ solutions, the blanks consisted of duplicate experiments in which distilled water was substituted for the salt solutions.
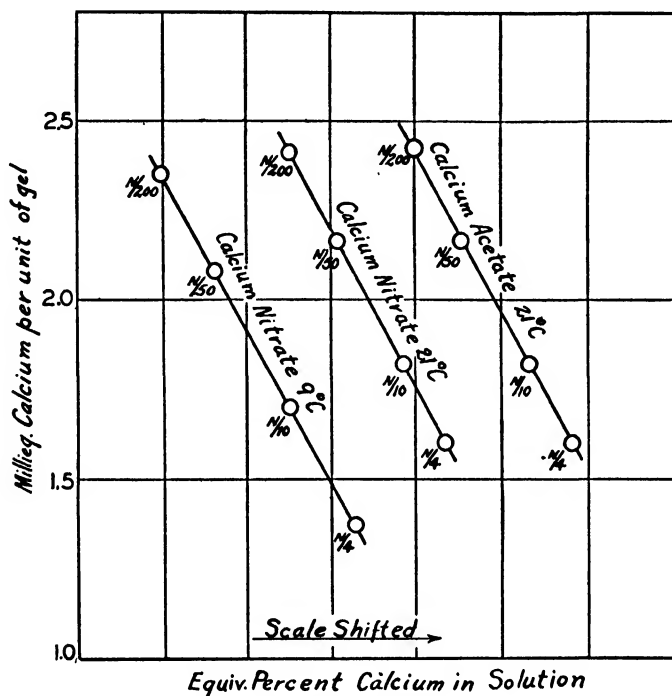
Fig. 2. *The effects of temperature and of anionic concentration upon the* $Ca^{++} \rightleftharpoons Na^+$ *reaction. (Initial ratio, calcium in solution : sodium in gel = 1.2 : 1).*

A pure calcium Doucil could not be prepared directly from sodium Doucil. Successive treatments with $N/2$ calcium nitrate solutions extending over 24 hr. gave a conversion of 69.7%, and a similar treatment with $N/1000$ solutions gave 80.7%. This value was raised to 90.2% when the treatments were continued for several weeks.

The ratio of the calcium in the initial solution to the sodium in the initial gel was kept constant at 1.2 : 1 in the experimental series that illustrate the effects of temperature and dilution. Under these conditions the points that were obtained for each series would lie on a straight line when plotted on a diagram similar to that given in Fig. 1. Similar lines are shown in Fig. 4 of the earlier paper.

The calcium-sodium curve at $N/4$ was obtained with pure calcium nitrate solutions and also with solutions of calcium and sodium nitrates. In the

latter, the ratios of the bases (sodium to calcium) varied from 0.1 to 50, and the weights of Doucil for the two series varied from 0.2 to 15 gm. Although the initial conditions were so different in these experiments a concordant set of results was obtained, and hence the solution volume was not important at constant anionic normality. However the $N/4$ calcium chloride curve and the various curves at $N/1000$ were obtained at constant volume for each curve. The three upper points on the calcium Doucil curve at $N/4$ were obtained with mixed solutions of different volumes, and the other points were obtained with sodium nitrate solutions and at constant volume. There is no break in the curve to indicate the change in the experimental conditions.
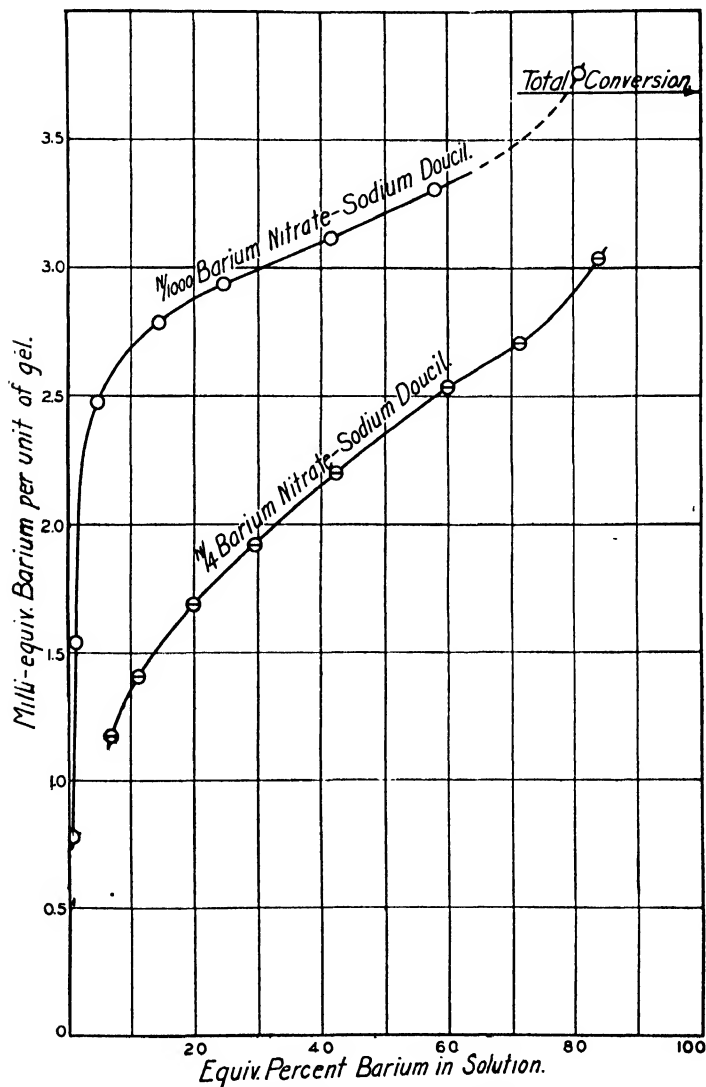
FIG. 3. *The Doucil base-exchange curves for the* $Ba^{++} \rightleftarrows Na^+$ *reaction at 21° C.*

In the presentation of the results, the base content and not the true cationic content is used; the former is considered as though it were identical with the latter. In Figs. 1, 2 and 3, the writers have plotted E'_1, the milli-equivalents of the entering cation in the final gel, against P, the equivalent percentage
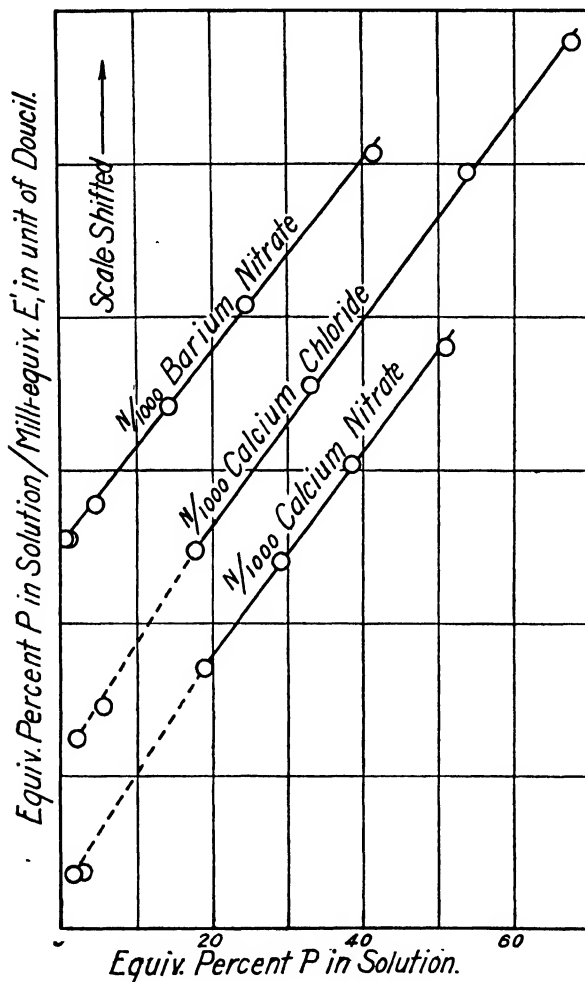
FIG. 4. -The barium and calcium base-exchange results at great dilution. (To illustrate the use of the equation $\frac{P}{E'_1} = a + bP$.)

(bases only) of this cation in the final solution. P may be defined as $\frac{E_1}{E_1 + E_2} \times 100$. The corresponding percentage $\frac{E'_1}{E'_1 + E'_2} \times 100$ for the gel is not a suitable variable because the gel capacity $(E'_1 + E'_2)$ is uncertain. At constant gel capacity, E'_1 is proportional to this percentage, and the use of it does not materially affect the shapes of the curves. In this way the functional relation that exists between the relative cationic content of the

final gel and of the final solution may be indicated, although the actual gel capacity may be unknown. The gel unit contained initially 3.68 milli-equivalents of sodium.

The calcium-sodium results are indicated in Fig. 1, and the barium-sodium results in Fig. 3. The temperature and dilution series for calcium-sodium are given in Fig. 2. Had the scale not been shifted, the lines would all pass through the point 100 on the abscissa. Fig. 4 shows the range of solution compositions over which the equation $P/E'_1 = a + bP$ is applicable at high dilution.

Discussion

The capacity of a gel for a particular base-exchange reaction must be obtained either from some direct measurement or from the exchange curve. Neither of these methods can be used with assurance. The curves are usually smooth over a wide range of P-values, but in many cases they turn up at their upper ends. There is no accepted method for the extrapolation of the central smooth portion, and the capacity that is obtained from experiments with successive treatments with the pure salt solutions may not be the proper capacity for this smooth part of the curve.

As the concentration of the solution decreases from $N/4$ to $N/1000$, the curves gradually change in shape and become similar to the curve for the $Ag^+ \rightleftarrows Na^+$ reaction. This was evident in the uni-divalent exchanges with copper, with calcium, and with barium. Since the $Ag^+ \rightleftarrows Na^+$ reaction was apparently independent of the concentration of the solution at such normalities, this trend is significant. The curves at the low concentrations are evidently a better measure of the true exchange reaction than are those for the higher concentrations. Some might regard the curves at $N/1000$ of dubious value, but they are supported by the results at the intermediate concentrations. If one extrapolates upward the $N/1000$ calcium nitrate curve, it cuts the axis at a point close to 3.03 milli-equivalents. The calcium content of the 80.7% calcium Doucil was 2.97 milli-equivalents. Since the former value was obtained from experiments of one and one-half hours' duration and the latter from an experiment lasting 24 hr., it is but reasonable to assume that the capacity for this curve is close to these values. It may be noted that a maximum conversion of 90.2% or 3.32 milli-equivalents was obtained in prolonged experiments and that the initial base content of the gel was 3.68 milli-equivalents. Neither of these values appears suitable, and the question of the capacity is apparently one that must be considered separately for each case. A similar treatment cannot be given the $N/4$ curves, since they do not appear to be single curves. The proper capacity cannot be determined for any portion of them. Extrapolation is a doubtful procedure, and the tendency of the curves to rise at their upper ends makes the capacity that is found by successive treatments with pure salt solutions of doubtful significance.

Many experiments suggest that the position of the exchange curve may be a rough gauge of the capacity. The relative positions of the curves are in

qualitative agreement with the conversions that are obtained with successive amounts of the pure salt solutions. Dilute solutions are better than strong ones, and copper enters the gel more readily than calcium. In one experiment, sodium Doucil was treated with successive amounts of $N/2$ cupric nitrate solution for 24 hr. (total), and this yielded a conversion to copper Doucil of 85.4%. This conversion was not increased by subsequent treatments with any other solution that was tried, including the $N/1000$. But the latter solution, when used initially, produced a 98% conversion in 24 hr. The calcium nitrate solutions under similar conditions gave conversions of 69.7 and 80.7% respectively.

If the position of the exchange curve be taken as an indication of the actual capacity, it follows that comparisons of the exchanging power of various cations are often comparisons of capacities. This is particularly true in those cases in which the curves flatten at high solution percentages, and the points selected for comparison are in this region. Renold's (2) comparisons are often of this type. Many have used the amount of added salt for one variable, instead of the equivalent percentage for the solution, which is used in this paper. Points are selected for comparison that correspond to the same amount of added salt, usually an amount equivalent to the base content of the gel. This method may be illustrated by Fig. 1. It is a comparison of the point on the upper curve at $P = 33.6$ with the point on the lower curve at $P = 62$. In general, one would expect this comparison to be more a function of the shape of the exchange curve in addition to the capacity than would be a comparison at a high value of P such as 70. This may be an advantage for some purposes, but this method of representing exchange results is open to the criticism that the important variables, the cationic content of the solution and of the gel are not both used, and the former is a function of the two variables that are used. Moreover the use of diagrams that are of the infinite type avoids the questions raised by the finite diagram, and hence minimizes the importance of the upper parts of the exchange curves and of the actual capacity.

Renold has concluded that many of his results with Permutite are best explained by the assumption that a certain blocking of the diffusion paths takes place in the gel. The writers believe that the available capacity for a given reaction is greatly affected by the ease with which the entering cation can enter the gel. The observations of the writers and of others seem to show that the ability to penetrate a gel is a specific property of the cation or cationic complex. The blockage of the diffusion paths also seems important, and no doubt plays an important part in the influence of temperature and of anionic concentration on the reaction, as indicated by the writers' various uni-divalent results. These matters are of utmost importance to those interested in the actual amount of exchange that takes place, but the available capacity and the exchange are different entities. The rules that govern these may have some qualitative similarities, but it is most unlikely that the rules are in any case identical. For example, the cationic hydration may be

an important factor in the penetration and in the exchange reaction, but a correlation between the extent of the hydration and the total amount of exchange does not necessarily yield accurate information about the exchange process at constant capacity.

The separate curves for the silver nitrate-sodium Doucil and for the sodium nitrate-silver Doucil reactions that were given in the first paper show that the solution composition at equilibrium is not uniquely defined by the base content of the gel, but is in addition dependent on the kind of gel that is used. The calcium-sodium results are similar, and somewhat similar observations have been made by Renold who attributed them to inner- and outer-held cations. It would seem likely that the diffusion paths are different in each pure gel, and that a large amount of exchange may take place without a corresponding change in gel structure. No doubt the water content of the gel is an important factor. The ideal case for the study of the exchange reaction would be one in which no structural changes occur in the gel. The practical difficulty is that in experiments of short duration the penetration of the gel may nót be constant for a series of different solutions containing the same cations, and that the nature of the gel may change in longer experiments. Although the experiments of Renold often lasted for days, it is evident that the uncertain capacity factor was not thereby eliminated.

Other factors that may affect the available capacity would be a competitive exchange with hydrogen, since aqueous solutions are used, and an exchange with the alumina in the gel. The latter seems a probable explanation of the very high points on some of the exchange curves. Renold states that a $N/2$ cupric chloride solution dissolves alumina from Permutite. The total solution of a part of the gel might so contaminate the solution as to affect the blocking of the diffusion paths in the gel and to alter the pH of the solution. In general one would expect such effects to be of minor importance.

The errors that are introduced by the use of the base content in the place of the cationic content are somewhat lessened by conducting the experiments at constant anionic normality, and by the fact that the relative cationic content of the solution is involved. The compensation, owing to the latter, no doubt accounts for the negligible influence of temperature on the silver-sodium exchange and on the calcium-sodium exchange at high dilution. It may also account for the apparent independence of concentration observed by the writers for the former reaction. However the elimination of a factor by compensation in certain cases does not constitute evidence that the reaction is in general independent of this factor.

The amount of exchange that takes place in a given case is influenced by so many factors that it is difficult to draw conclusions concerning the nature of the true base-exchange reaction, that is, the reaction at constant capacity with the same type of gel material. The writers' results suggest that the composition of the gel is determined by the relative cationic content of the solution if disturbing factors be eliminated. This is in accord with the opinions of Rothmund and Kornfeld (3) and of Verwey (4). The former

consider the reaction as chemical, while the latter treats it as an adsorption process. The effects of temperature are probably small or negligible owing to compensation, and the effects of anionic concentration on uni-univalent exchanges are probably of the same kind.

In the uni-divalent exchanges, the anionic concentration has a marked effect on the total amount of exchange that takes place with salt solutions. Qualitative evidence indicates that this is, at least in part, due to a change in available capacity. The Rothmund and Kornfeld equation as applied to the barium-sodium exchange would be

$$\left(\frac{\text{Na}^2}{\text{Ba} \cdot V}\right)_{Soln.} = K \cdot \left(\frac{\text{Na}^2}{\text{Ba} \cdot V}\right)^P_{gel} \cdot$$

Na and Ba represent the amounts of these bases in the volume V. From this, it follows that the ratio $\dfrac{\text{Na}^2}{\text{Ba}}$ for the solution is proportional to the volume of the solution at constant gel composition and capacity. It also follows that the barium in the solution must decrease as the volume increases. The latter deduction is in accord with the observations given in Fig. 3. But if one compares the results at $N/1000$ with the results at $N/4$, at constant gel composition, the ratio $\left(\dfrac{\text{Na}^2}{\text{Ba}}\right)_{Soln.}$ is so far from being proportional to the volume of the solution that it is very questionable whether this equation is of the right type. For a gel that contains 25 milli-equivalents of barium, the volume ratio for $N/1000$ and $N/4$ is 250, and the ratio of the two $\left(\dfrac{\text{Na}^2}{\text{Ba}}\right)_{Soln.}$ terms is 11.6. Somewhat similar discrepancies were found for gels containing 15 and 20 milli-equivalents of barium. Were it possible to compare these results, for a constant capacity, the two exchange curves would be brought closer together and the discrepancy increased. It would seem likely that the greater part of the differences between these two curves might disappear if a proper correction could be made for the capacities. The curves are much closer together in the case of the barium-sodium reaction than in the other uni-divalent reactions, and a search is being made for a reaction in which they might be even closer together.

In Fig. 4, the lines indicate the usefulness of the equation $P/E'_1 = a + bP$ for the expression of the results at great dilution. The exchange curve must flatten at high solution percentages if it agrees with this equation. Either the equation is not suitable for the whole range or the curve is distorted by some factor such as a variable capacity. For the present, it would seem best to regard the equation as merely a convenient equation for the interpolation of results in certain ranges of solution percentages. The barium nitrate results and Musgrave's silver nitrate results (1) show that it may be useful at low or at high solution percentages in some cases. It does not agree so well with the results that are obtained at the higher normalities such as N/4 for the uni-divalent exchange reactions. These results yield curves that change direction and rise rapidly as the solution percentage approaches 100.

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THE BROMINE-SENSITIZED DECOMPOSITION OF CHLORINE MONOXIDE IN GREEN LIGHT[1]

BY A. G. BROWN[2] AND J. W. T. SPINKS[3]

Abstract

Chlorine monoxide undergoes a bromine-sensitized decomposition in light of wave-length 5460 A. The reaction involves short chains and is accompanied by an appreciable dark reaction. The quantum yield is 4.3 at 19° C. A decrease in pressure occurring near the end of the reaction has been shown to be a photochemical effect, and it is due probably to the bromine-sensitized decomposition of chlorine dioxide formed during the combined light and dark reactions.

A mechanism similar to that described by Finkelnburg, Schumacher and Stieger for the unsensitized reaction appears to account for most of the observations.

Introduction

The photodecomposition of gaseous chlorine monoxide has been investigated quantitatively by E. J. Bowen (5) and by Bodenstein and Kistiakowsky (4). The rate of decomposition was found to be proportional to the amount of light absorbed, and the observed quantum yield of 2 was the same, irrespective of whether chlorine or chlorine monoxide absorbed the light. The reaction was not affected by the presence of air or oxygen, and chlorine dioxide was shown spectroscopically to be present in increasing amounts as the reaction proceeded. It was suggested that excited molecules of chlorine monoxide or chlorine were responsible for the decomposition. However, Bodenstein and Kistiakowsky (4) and Goodeve and Wallace (12) showed that the absorption spectrum of chlorine monoxide was continuous between 6200 Å and 2300 Å. Thus, following the work of Franck (10) and others it appeared probable that light absorption in this region resulted in the dissociation of the molecule. A reaction mechanism involving such a dissociation and accounting for the observed quantum yield of 2 was proposed by Schumacher and Wagner (25).

$$Cl_2O + h\nu \longrightarrow ClO + Cl$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO \ (+ \ 14 \ Cal.)$$
$$ClO + ClO \longrightarrow Cl_2 + O_2 \ \ (+ \ 74 \ Cal.)$$
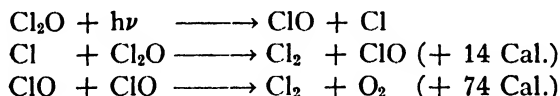
The mechanism suggested for the sensitized reaction was:

$$Cl_2 + h\nu \longrightarrow Cl + Cl$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO$$
$$ClO + ClO \longrightarrow Cl_2 + O_2.$$
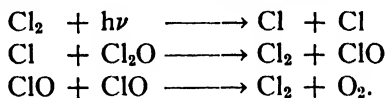
The gaseous reaction was reinvestigated by Finkelnburg, Schumacher and Stieger (9). They determined the extinction coefficient of chlorine monoxide over the continuous range 6700 to 2200 Å. Four maxima were found in the

region of continuous absorption. The first sharp maximum at 6250 Å (45.5 Cal.) was thought to involve dissociation;

$$Cl_2O \longrightarrow ClO + Cl \; (43.5 \; Cal.).$$
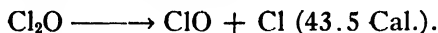
The second and third maxima at 5320 Å and 4290 Å were considered to correspond to dissociation into excited products, ClO and Cl. Absorption in the last broad maximum at 2560 Å (93 Cal.) resulted in dissociation into separate atoms,

$$Cl_2O \longrightarrow Cl + Cl + O.$$

Quantum yields were determined for purified dry chlorine monoxide at the wave-lengths 4360, 3650 and 3130 Å. The mean quantum yield for 3650 Å was 3.5 (10° C.) and the mean temperature coefficient 1.12. Chlorine dioxide and higher unknown oxides were shown to be present. The mechanism of Schumacher and Wagner, as outlined, was extended to explain quantum yields greater than 2. Such higher yields were considered to be due to reactions leading to chain formation *e.g.*,

$$ClO + Cl_2O \longrightarrow Cl + Cl_2 + O_2 \; (+ \; 31.5 \; Cal.).$$
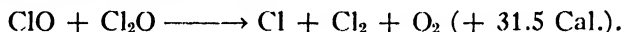
These will be discussed further.

Subsequently, Schumacher and Townend (24) reinvestigated the region of dissociation into atoms. The observed quantum yield of 4.5 at 2500 Å was thought to be due to the primary process

$$Cl_2O + h\nu \longrightarrow Cl + Cl + O,$$
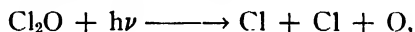
followed by the series of reactions described by Finkelnburg, Schumacher and Stieger.

The thermal decomposition of chlorine monoxide has been investigated by Hinshelwood and Prichard (15), Hinshelwood and Hughes (14) and by Beaver and Stieger (3). Chlorine dioxide again appeared to be formed as an intermediate product, and it seems probable that, apart from the primary action, the mechanisms of the photo and thermal reactions are very similar.

In view of the work already done, the bromine-sensitized decomposition of chlorine monoxide was undertaken. With bromine, green light can be used which produces excited bromine molecules. The reaction of the latter with chlorine monoxide can be studied, and should be of particular interest since very few definite cases of molecular sensitization are known. A comparison with the chlorine-sensitized reaction (where atoms are involved) should also be possible.

Experimental

Materials

Chlorine monoxide was prepared by passing dry chlorine, either pure or mixed with dry air, over specially prepared mercuric oxide in a water cooled tube. The mercuric oxide was prepared by precipitation from saturated mercuric chloride solution with 50% caustic. After a thorough washing with distilled water, it was collected and dried at 110–120° C. for at least 12 hr. In the preliminary experiments tank chlorine was used, but since the resulting

chlorine monoxide showed a very large dark reaction, the tank chlorine was replaced by chlorine generated from potassium permanganate and hydrochloric acid. Before passing the chlorine over the mercuric oxide, it was purified by bubbling it through potassium permanganate solution, and then dried with concentrated sulphuric acid and phosphorus pentoxide.

The chlorine monoxide from the generating tube was mixed with bromine and drawn into the reaction cell. Since others have shown that the photoreaction is not affected by air, oxygen or chlorine, no attempt was made at this stage to prepare pure chlorine monoxide.

Methods of Analysis

The composition of the gaseous mixture was found either by analyzing the contents of a bulb of known volume filled at the same time as the reaction cell, or by analyzing the contents of the cell itself. In either case the gas was passed, by means of a stream of dry air, into neutral potassium iodide solution.

$$Br_2 + 2\ I^- \longrightarrow I_2 + 2\ Br^-$$
$$Cl_2 + 2\ I^- \longrightarrow I_2 + 2\ Cl^-$$
$$Cl_2O + 4\ I^- + H_2O \longrightarrow 2\ I_2 + 2\ Cl^- + 2\ OH^-$$
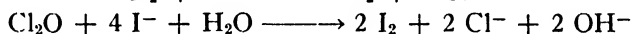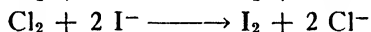
After acidifying with a known amount of $0.1\ N$ sulphuric acid, the solution was titrated with standard thiosulphate. The titration gave a measure of the total bromine, chlorine and chlorine monoxide. Excess of $0.1\ N$ potassium iodate was then added and the iodine titrated.

$$IO_3^- + 6\ H^+ + 5\ I^- \longrightarrow 3\ I_2 + 3\ H_2O$$
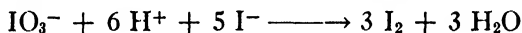
The difference between this titre and the thiosulphate equivalent of the $0.1\ N$ sulphuric acid originally added gave the equivalent of the OH^- produced by the reaction of chlorine monoxide and the iodide solution. Hence, the concentration of chlorine monoxide could be calculated. In some cases the chlorine monoxide concentration was obtained from the total increase in pressure at total decomposition.

The bromine concentration may be obtained from the percentage absorption of 5460 Å and an absorption curve for this wave-length. For concentrations of chlorine monoxide sufficient to give an appreciable absorption of 5460 Å it would be necessary to allow for its absorption.

Apparatus and Procedure

Two similar cylindrical cells of Suprax glass, 10 cm. in length and 5 cm. in diameter, with plane ends, were used. The cells and all connecting tubes were immersed in a
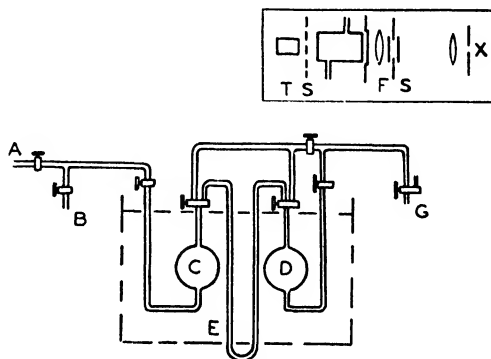
FIG. 1. *Apparatus. A, chlorine monoxide inlet; B, bromine inlet; C and D, light and dark reaction cells; E, manometer; G, tube leading to analysis bulbs and water pump. Inset—optical arrangement: T, thermopile; S,S, shutters; F, light filter; X, mercury lamp.*

constant temperature bath kept at 19° C. (Fig. 1). The reaction

$$2 \, Cl_2O \longrightarrow 2 \, Cl_2 + O_2$$
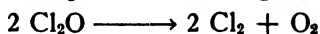
takes place with an increase in volume. Consequently the course of the reaction was followed by means of a sulphuric acid manometer connected between the cells and read to 0.001 cm. by means of a cathetometer. Taps were lubricated with concentrated sulphuric acid.

Light from a quartz mercury lamp (1.8 amp.) was limited by a 1 cm. diaphragm, and after passing through light filters was made nearly parallel by means of a large semiconvex lens. Then the light was directed, by means of a second convex lens, through a window in the thermostat and into the cell. The whole of the slightly converging beam fell on the surface of a thermopile. A shutter could be interposed between the cell and the thermopile. This allowed readings of light intensity to be made from time to time during the run (Fig. 1, inset).

The wave-length of 5460 Å used in the experiments was obtained by means of a combination of Corning Nonex, heat-resisting yellow glass, 2.8 mm. thick, and a Corning Didymium glass 4.97 mm. thick. This arrangement, together with the light from a mercury arc, gave a source of light of wave-length 5460 Å. The wave-length 3650 Å used in some experiments was obtained by means of a Corning Red Purple Ultra Filter, 3.9 mm. thick.

Energy measurements were made by means of a 2 cm. Moll surface thermopile, stepped down and blackened (23), connected in series with a moving coil galvanometer which had an optical lever of 1.2 m. radius.

The thermopile was calibrated by means of a carbon filament lamp from the Bureau of Standards, Washington, D.C. It was found that 1 mm. scale deflection corresponded to 1.0903×10^{-5} watts per sq. cm.; equivalent to 1.988×10^{15} quanta per minute at 5460 Å and 1.329×10^{15} quanta per minute at 3650 Å, after making a reflection correction of 9.3% (2, p. 1658).

Using the equation $PV = NRT$, an expression may be obtained relating the change in the number of molecules of gas with the movement of the manometer liquid (2, p. 1658). When $V = 186$ cc., $T = 19°$ C., $P = 715$ mm. and the diameter of the capillary manometer is 1.83 mm.; 1 mm. sulphuric acid $\equiv 8.5 \times 10^{17}$ molecules, a slight correction being made for volume change due to the movement of sulphuric acid in the manometer. Since a change in volume of one mole represents the decomposition of two moles of chlorine monoxide the expression for the quantum yield, γ, reduces to:

$$\gamma_{5460} = \frac{2 \times 8.5 \times 10^{17} \times \text{mm. sulphuric acid per min.}}{1.988 \times 10^{15} \times \text{mm. deflection}}$$

$$\equiv 8.55 \times 10^2 \times \frac{\text{slope of rate curve}}{\text{mm. light absorption}}$$

Results

In several preliminary experiments a fast and unexpected thermal reaction occurred whose rate was considerably reduced when the tank chlorine (used in the preparation of chlorine monoxide) was replaced by chlorine prepared by the interaction of hydrochloric acid and potassium permanganate.

However, when bromine was added to chlorine monoxide a slow dark reaction still took place, and became increasingly faster in subsequent experiments. After a number of runs the reaction cell was cut down and washed out with a few drops of water. The solution so obtained gave tests for ClO_3^- (characteristic diamond-shaped plates of potassium chlorate with potassium chloride solution) and ClO_4^- (typical crystal clusters with 2% brucine in dilute acetic acid). These results indicate the presence of Cl_2O_6 which reacts with water according to the equation.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
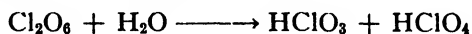
By cleaning the cell at intervals the thermal reaction rate was kept quite low compared to the rate of the photo reaction (0 to 15%). The true rate of the photo reaction was determined by subtracting the mean rate of the thermal reaction (before and after the experiment) from the total reaction rate during insolation. A typical pressure-time curve is shown in Fig. 2 (a).
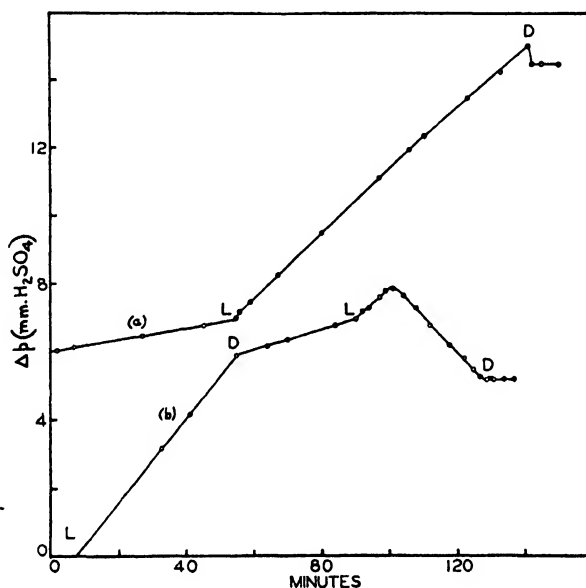
FIG. 2   *Typical pressure-time curves.*

On insolation there was a small Budde effect, after which the pressure increased steadily. When the light was cut off an inverse Budde effect was produced, and the pressure then increased more slowly owing to the small thermal reaction. Upon re-insolation the increase in pressure continued at the former rate.

Toward the end of the reaction ($Cl_2O < 0.25\%$) an unexpected effect was observed. In a period of less than five minutes, the normal pressure increase changed over into a pressure decrease. On cutting off the light, the pressure remained constant. This indicated that the effect was photochemical. The pressure decrease continued on further insolation and was thought to be due

to a condensation of a relatively non-volatile substance such as Cl_2O_6 on the walls of the vessel (Fig. 2 (b)). After a further period of insolation the pressure began to increase again, and it continued to increase until all the chlorine oxides had decomposed. The effect was first observed with light of wave-length 5460 Å and mixtures containing bromine. A similar effect was observed for bromine-free mixtures and the wave-length 3560 Å*.

From the rate of decomposition (as measured by the slope of the pressure-time curve) and the number of absorbed quanta, the quantum yield was calculated. While the above-mentioned irregularities would seem to make the exact magnitudes of the quantum yields somewhat uncertain, the values obtained in the early period of the reaction were all approximately equal to 4 over a range of concentrations of chlorine monoxide from 0.35 tb 5.0% and bromine from 1 to 6% (from 20 to 75% absorption of 5460 Å). The mean value of γ_{5460} for the sensitized experiments was 4.3, the possible error being about 10% (Table I).

Quantum yields for the unsensitized photodecomposition of chlorine monoxide were also determined. A dark reaction again appeared as a variable and complicating factor, and the mean value of γ_{3650} for the unsensitized reaction was found to be 5.3 at 19° C. This is somewhat higher than the value obtained by Finkelnburg and co-workers (9).

TABLE I

QUANTUM YIELDS FOR THE BROMINE-SENSITIZED
REACTION AT 5460 Å

Chlorine monoxide-bromine mixtures (plus chlorine and dry air) at 19° C.
Total pressure, 710 mm. of mercury.

Chlorine monoxide by volume, %	Light absorbed (by bromine), %	Quantum yield
0.32	57.0	5.2
0.35	19.3	4.1
0.59	58.2	4.7
0.70	51 6	3.5
0.91	58.6	4.0
1.02	61.0	4.4
1.2	65.5	4.1
1.39	66.1	3.9
2.3	22.2	5.3
3.1	23.1	4.3
5.0	60.0	4.4
5.5	31.0	4.8
6.3	37.4	4.2 ·
		Mean 4.3

Their value $\gamma_{3650} = 3.5$ at 10° C. and a temperature coefficient 1.12 leads to $\gamma_{3650} = 4$ at 19° C. It is possible that the difference may be due either to the dark reaction or to the low concentration of chlorine monoxide.

The ratio $\dfrac{\gamma_{3650} \text{ (unsensitized)}}{\gamma_{5460} \text{ (sensitized)}} = \dfrac{5.3}{4.3} = 1.2$. From the values of γ for different wave-lengths in Schumacher's paper (9, p. 145) one can estimate that for the unsensitized reaction, $\dfrac{\gamma_{3650}}{\gamma_{5460}} = 1.3$. Therefore the ratio $\dfrac{\gamma_{5460} \text{ (sensitized)}}{\gamma_{5460} \text{ (unsensitized)}} = 1.08$.

While the accuracy is not very great, one can safely say that the quantum yields for the sensitized and unsensitized reactions are practically equal. The equality of the quantum yields obtained in these experiments suggests

* *Finkelnburg and co-workers (9) record a sharp rise in pressure at the end of one of their experiments.*

that, apart from the primary act of light absorption, the sensitized and un-sensitized reactions have essentially similar mechanisms. The reaction thus shows a close resemblance to the chlorine-sensitized decomposition of chlorine monoxide (4) and the bromine-sensitized decomposition of chlorine dioxide (27).

Experiments were attempted with water covering the bottom of the reaction cell, using bromine and chlorine monoxide mixtures. An extremely rapid increase in pressure was observed in the dark, the rate decreasing slightly on insolation with light of wave-length 5460 Å. Because of the magnitude of the dark reaction, further investigation in this direction seemed unprofitable.

Discussion

Primary Effect of Light Absorption

While 5460 Å is well within the continuum for chlorine monoxide, the extinction coefficient at this wave-length is very low. In a preliminary experiment with chlorine monoxide at a partial pressure of 304 mm. of mercury, the absorption of 5460 Å by a 10 cm. thickness was 18.6%. This is in good agreement with the value given by Goodeve and Wallace (12), and shows that, in the sensitized experiments, even the highest concentrations of chlorine monoxide used (40 mm. of mercury) would absorb less than 3% of the incident light at 5460 Å. In most experiments the absorption of the incident light by chlorine monoxide would be less than 1%. This was verified by direct measurement. Consequently, in the bromine-sensitized reaction the light is being absorbed almost exclusively by the bromine.

Since the mixture contains chlorine the possibility of BrCl formation has also to be considered even at the beginning of an experiment. The equilibrium constant K for the reaction $2BrCl = Br_2 + Cl_2$ is 0.107 at 28° C. (30). If the heat of formation given by Jost (16) is used, the value of K at 19° C. is 0.111, which corresponds to the formation of a relatively large percentage of BrCl, the percentage naturally depending on the concentrations of bromine and chlorine.

According to Vesper and Rollefson (30), bromine and chlorine react com-paratively slowly in the dark, but this result is contradicted by Jost (17) and by Brauer and Victor (6) who find a rapid reaction. The reaction rate is accelerated by light (absorption in the band and continuous regions being equally effective) and the photoreaction has a quantum yield of about 10^3. It is of course quite possible that the reaction may be strongly inhibited by chlorine monoxide.

Gray and Style (13) mention that the transmission of 5460 Å by mixtures of bromine and chlorine is unaffected by insolation with 5460 Å, and that the extinction coefficient of BrCl is very small compared to that of bromine at the same wave-length $\left(\dfrac{\alpha BrCl}{\alpha Br_2} = \dfrac{1.2}{29.6} \text{ at } 5460 \text{ Å} \right)$. Thus, in these experi-ments the light is being absorbed almost exclusively by bromine.

The main continuum for bromine begins only at 5107 Å, and it is therefore evident that the primary process of light absorption at 5460 Å results in the formation of excited bromine molecules. It should perhaps be mentioned that there is a faint underlying continuum extending to at least 6400 Å, and that absorption in this continuum would lead to dissociation into normal atoms (1,7). However, from the relative intensities of the underlying continuum and the main band system, it appears probable that the fraction of bromine molecules dissociating directly, as a result of light absorption at 5460 Å, is small. The fact that 5460 Å excites fluorescence in bromine (20) also supports the hypothesis that excited bromine molecules are formed.

There is of course the further possibility that excited bromine molecules dissociate on collision with another bromine molecule or with a foreign molecule. Rabinowitch and Wood (21, 22) give experimental proof that, in the case of iodine, all excited iodine molecules dissociate because of collisions with foreign molecules. They also consider that the observations of Jost on the bromine-hydrogen reaction in the band and continuous regions of the bromine spectrum make it probable that a great number of primarily excited bromine molecules dissociate into atoms by collisions with hydrogen and bromine molecules. The reactions of bromine with ozone (26), platinum (29), cyclohexane (18), chlorine dioxide (27) and chlorine (6), show a similar behavior.

Mechanism of the Sensitized Photoreaction

If the secondary production of bromine atoms is postulated, the first part of the reaction can be represented by the following:

$$Br_2 + h\nu \longrightarrow Br_2{}^*$$
$$Br_2{}^* + M \longrightarrow Br + Br + M$$
$$Br + Cl_2O \longrightarrow BrCl + ClO \; (+ 8.7 \; Cal.)$$
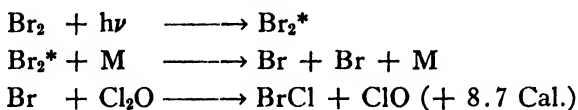
ClO would then react further with chlorine monoxide (see below). The ratio of BrCl formed to chlorine monoxide decomposed would be in the ratio $2 : \gamma$, *i.e.*, about 2 : 4 in the authors' experiments. Since the extinction coefficient of BrCl differs from that of bromine at 5460 Å (see above), an increase in light transmission at this wave-length would be expected. Actually none was observed, but the situation is complicated by the fact that BrCl decomposes into bromine and chlorine to form an equilibrium mixture. If this equilibrium were rapidly established (possibly accelerated by bromine atoms), the net removal of bromine as BrCl would not be as great as suggested by the above equations. The evidence in favor of the reaction proceeding by way of bromine atoms is thus rather inconclusive.

The other possibility is that the primarily excited bromine molecules collide with a chlorine monoxide molecule and decompose it. The decomposition of chlorine monoxide requires 43.5 Cal. and the quantum at 5460 Å corresponds

to 52 Cal. Hence a decomposition in this manner is energetically possible and may be represented by the following equations:

$$Br_2 + h\nu \longrightarrow Br_2^* \tag{1}$$
$$Br_2^* + Cl_2O \longrightarrow Br_2 + Cl + ClO \tag{2}$$
$$Cl + Cl_2O \longrightarrow Cl_2 + ClO \; (+ 14 \; Cal.) \tag{3}$$
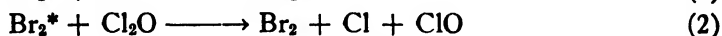
It is of course possible that an excited chlorine monoxide molecule is first formed and then splits up or reacts with another chlorine monoxide molecule. However, the first possibility would be indistinguishable from Reaction 2, and the similarity of the sensitized and unsensitized reactions makes the reaction $Cl_2O^* + Cl_2O \longrightarrow 2\,Cl_2 + O_2$ unlikely.

If the above mechanism is accepted, the observed quantum yields force one to conclude that energy exchange between bromine and chlorine monoxide molecules is quite specific, and takes place at practically every collision. At the same time the probability of an excited bromine molecule losing its energy on collision with foreign molecules such as oxygen or nitrogen must be small. A similar specific energy transfer occurs in the bromine-sensitized decomposition of chlorine dioxide (27). The importance of the nature of the colliding partner for deactivation of molecules activated by light is discussed by Franck (11), who concludes that collisions will be particularly efficient for dipoles and radicals. It is perhaps significant that chlorine monoxide has a dipole moment of 0.78×10^{-18} (28), while oxygen and nitrogen have zero dipole moments.

Quantum yields greater than 2 might result from the following reactions suggested by Finkelnburg, Schumacher and Stieger (9):

$$ClO + Cl_2O \longrightarrow Cl + Cl_2 + O_2 \; (+ 31.5 \; Cal.) \tag{4}$$
$$ClO + Cl_2O \longrightarrow ClO_2 + Cl_2 \; (+ 30 \; Cal.) \tag{5}$$
$$ClO + Cl_2O \longrightarrow 2\,ClO + Cl \; (- 43 \; Cal.) \tag{6}$$
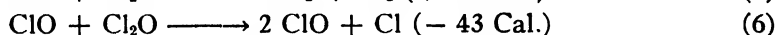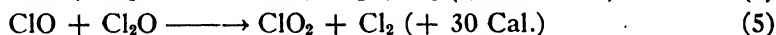
Of these, Reaction 6 is certainly infrequent. Reaction 5 has been shown to take place in the unsensitized reaction, and it is probably also responsible for the end effects in the sensitized reaction. Reaction 4 would provide the chain mechanism necessary to account for the observed quantum yields.

The chains must be terminated rather rapidly by the following reactions, but it is not yet possible to estimate their relative importance.

$$Cl + Cl + M \longrightarrow Cl_2 \tag{7}$$
$$ClO + ClO \longrightarrow Cl_2 + O_2 \; (+ 74 \; Cal.) \tag{8}$$
$$Cl + ClO + M \longrightarrow Cl_2O \tag{9}$$
$$Cl + ClO_2 \longrightarrow Cl_2 + O_2 \; (+ 55 \; Cal.) \tag{10}$$

The Pressure Decrease

There remains to be explained the decrease in pressure observed at the end of the reaction. This was proved to be a photoeffect and the experiments also suggested that some substance was separating out on the walls. Since chlorine dioxide is formed (Reaction 5), it seems probable that the bromine-

sensitized decomposition of this oxide takes place. This reaction has been shown to occur with a decrease in pressure at 16° C. owing to the separation of Cl_2O_6 on the walls (27). That this is the cause of the decrease in pressure observed at the end of the authors' experiments is supported by the chlorate and perchlorate formation described previously, and by the shape of the curves obtained on further insolation. It seems necessary to assume, however, that chlorine dioxide accumulates during the first part of the reaction, and that there is a preferential decomposition of chlorine monoxide as long as it is present in appreciable quantity†.

Since the wave-length 5460 Å does not come within the predissociation region for chlorine dioxide, the following reactions have been suggested:

$$Br_2 \ + \ h\nu \ \longrightarrow Br_2{}^*$$
$$Br_2{}^* \ + \ ClO_2 \longrightarrow ClO_2{}^* + Br_2$$
$$ClO_2{}^* + \ ClO_2 \longrightarrow ClO_3 \ + ClO$$
$$ClO_3 \ + \ ClO_3 \longrightarrow Cl_2O_6 \quad \text{(on walls)}$$
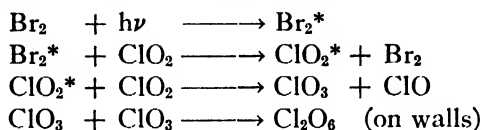
Other reactions of ClO and ClO_2 may also take place. The subsequent increase in pressure is due to the photodecomposition of Cl_2O_6 (27).

It is of particular interest to note that while the secondary production of bromine atoms is not entirely excluded, the bulk of the evidence favors sensitization by excited bromine molecules. Examples of reactions that are definitely of this type are extremely rare for unsensitized reactions†† and almost as rare for sensitized reactions, particularly where the sensitizer is a molecule.

Whereas excited atoms (mercury atoms, for example) usually sensitize a reaction by transferring their energy to molecules or atoms by collisions of the second kind, most molecular sensitizers play an active chemical role, the original sensitizing molecules being regenerated during the course of the reaction.

From the foregoing it is seen that, apart from the primary process of light absorption, the sensitized and unsensitized reactions have essentially similar mechanisms. The photoreaction is rather complicated and the unsensitized reaction needs to be investigated further before any more work on the bromine-sensitized reaction is undertaken.

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† *Compare the observations of Dickinson and Jeffreys (8) on the decomposition of chlorine monoxide in solution.*
†† *Compare the remarks of Norrish and Kirkbride (19).*

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THE VARIATION OF THE SULPHUR CONTENT OF WOOL[1]

By P. Larose[2] and A. S. Tweedie[3]

Abstract

The results obtained by other investigators which have a bearing on the variability of the sulphur content of wool are reviewed briefly. The variability of the sulphur content is discussed on the basis of the various factors that might affect it.

The effect of light is appreciable and is a very important one. Any sulphuric acid formed by the action of light, or present owing to some other cause, is difficult to remove by ordinary washing. The effect of boiling water is small. Kempy fibres contain less sulphur than non-kempy fibres of the same wool. The root portions of fibres have a higher sulphur content than the tip portions, while middle portions have intermediate values.

The writers' results and those of other investigators which are reproduced do not allow of any definite relation being drawn between sulphur content and fineness.

Introduction

The variability of the sulphur content of wool has engaged the attention of a number of investigators interested in the composition of wool. The diverse and often contradictory results obtained by various workers have resulted in differences of opinion regarding the extent of the variation in sulphur content and its relation to those factors capable of influencing it. These factors can be divided into internal and external, the internal factors being those that determine the process by which the wool fibre is formed in the follicle, whereas the external factors are those that act on the wool fibre outside the follicle. Differences of sulphur content between wools of various breeds, between wools of different fineness or between kempy and non-kempy wool would be due to the first-mentioned factors. The most important factors are probably the composition of the feed and the plane of nutrition. Among the external factors are the action of light and any action that the suint, wax or other substances present in the raw wool may exert.

Since in actual practice the effect exerted by the external factors on the various wools would vary in degree, it is difficult to correct for it when attempts are made to correlate the sulphur content with the internal factors. This may account for some of the differences in results obtained by various investigators.

The writers were interested in the variability of the sulphur content of Canadian wools, and they used the method described by Larose and Tweedie (10). They were interested also in carrying out sulphur determinations on a number of these wools and to a limited extent in verifying relations found by previous investigators.

Effect of Light Exposure

The decomposition of wool by light with the resulting decrease in sulphur content has been recorded. Barritt and King (3) exposed wool to the light of a quartz lamp for 80 to 100 hr. and found losses in sulphur varying from 3.7 to 5.0% of the original sulphur content, but these losses were larger (9.0 to 13.1%) when the wool was washed, after exposure, in a 0.001 N sodium hydroxide solution. Barritt and King showed that this dilute alkali treatment did not affect the sulphur content of normal wool. Mossini (12) reported a loss of 2.4% after exposing a sample of Australian wool to sunlight for 50 hr., but the losses were very much greater when the wool was subsequently treated with various solutions. Treatment in lime water after exposure gave the greatest loss (84%). This extraordinarily large loss is due, no doubt, not only to the action of light but also to that of the lime water on the wool.

Tests of a similar nature were conducted by the writers on samples of low $\frac{1}{4}$ Leicester wool that were exposed, one uncovered and the other under glass, for 132 hr. in sunlight. The results are given in Table I.

TABLE I

EFFECT OF EXPOSURE TO LIGHT ON SULPHUR CONTENT

Low $\frac{1}{4}$ Leicester wool. Original sulphur content, 3.47%

Treatment	Sulphur, %	Loss, %
Sample under glass for 132 hr. and exposed to sunlight *(A)*	3 30	4.9
A washed in several changes of water and one hour in 0.001 *N* sodium hydroxide	3.10	10.7
Sample uncovered and exposed to sunlight for 132 hr. *(B)*	3.30	4.9
B washed in several changes of water and one hour in 0.001 *N* sodium hydroxide	2.85	18.2

These results show changes of the same order as those reported by Barritt and King. The smaller loss in sulphur content of the wool covered by glass during exposure is due probably to a reduction in intensity of the light of shorter wave-lengths in passing through the glass.

Another sample that had been exposed for 96 hr. in a fugitometer but that was not subsequently washed with dilute alkali showed a loss too small to be significant, probably owing to a different distribution of light energy and to the unfavorable condition of low humidity obtaining at the time of test.

Effect of Absorbed Sulphuric Acid.

In connection with the test on exposure to light, an experiment was carried out to determine the extent to which any sulphuric acid in the wool was removed by the ordinary water rinsing. A sample of wool was treated with a 1% sulphuric acid solution according to the procedure adopted by Wilkinson and Tyler (16, p. 370) in their work on the absorption of acids by wool. The

original sulphur content of the wool was 3.58%. After the acid treatment the value found was 3.76%, corresponding to an "acid retained" value of 0.54%, a value somewhat lower than the 0.7% reported by Wilkinson and Tyler. The wool was subjected to a further rinsing in running warm distilled water of pH 5.5 for six hours, and this reduced the sulphur value to 3.69%, corresponding to an acid retention of 0.33%. It is, therefore, difficult to remove all sulphuric acid by water alone, and this should be borne in mind when a determination is made of the sulphur content of wool suspected of containing sulphuric acid.

Effect of Boiling Water

It has been observed by Clayton (8) that when wool is heated in boiling water, hydrogen sulphide is given off, although the quantity is very small and the evolution is said to cease after a short time. The extent of such evolution was determined by analyzing for sulphur content, before and after the treatment, a sample of Welsh wool that was boiled for five two-minute periods, the water being changed between each boiling. The sulphur was also determined for a sample that had been subjected to a further boiling for one hour. The results are given in Table II.

TABLE II

EFFECT OF BOILING ON SULPHUR CONTENT OF WOOL

Original sulphur content, 4.12%

Treatment	Sulphur, %
After boiling five two-minute periods	4.07
After boiling one hour more	4.04

These figures indicate that there is an appreciable loss of sulphur on boiling with water, but that most of this loss occurs during the initial stages, in confirmation of previous observations.

Sulphur Content of Kempy Fibres

That kempy fibres have a lower sulphur content than non-kempy fibres from the same wool has been shown by Barritt and King (2), who reported values of 3.82, 3.33 and 3.24% for fine non-kempy wool, coarse kempy wool and kemps, respectively, in a sample of Black Face wool. They used these figures to show (4) that the medulla from kempy fibres was free of sulphur. Bekker and King (5) worked with porcupine quills and carried out a partial separation of the cortex from the medulla. By direct determination they found a lower sulphur content in the medulla than in the cortex. That the medulla showed an appreciable sulphur content was attributed to incomplete separation of the cortex from the medulla. Staining methods, applied to cross sections of wool fibres as well as porcupine quills, seemed to show the absence of sulphur in the medulla. Jordan-Lloyd and Marriott (9) found that the medulla could be separated from the cortex in goat hair by treatment with 4 N sodium hydroxide solution, and they took advantage of this to carry out sulphur determinations in the cortex and medulla separately. A sulphur content of 3.60% was found for the cortex and 0.23% for the medulla.

These results show that if the medulla is not entirely free of sulphur, its sulphur content is at least much lower than that of the cortex, and they explain why kempy fibres should be found to have a lower sulphur content.

Table III gives the results obtained by the writers which are in agreement with those previously reported.

The agreement between individual determinations on the samples listed in Table III was not so good as that usually obtained. This was to be expected in view of the wide variation in the kempiness of the fibres.

TABLE III
SULPHUR CONTENT OF KEMPY FIBRES

Sample	Sulphur, %
Original wool	3.45
Kempy fibres from original wool	3.36
Non-kempy fibres from original wool	3.55
Kempy fibres from fine locks in original wool	3.56
Non-kempy fibres from fine locks in original wool	3.68
Kempy fibres from coarse locks	3.34

Variation Along the Fibre

The wool fibres have been divided at times into two or three distinct portions, generally into base, middle and tip portions in order to determine the variation of the sulphur content along the fibres. This variation, as found by various investigators, was not always in the same direction. Bonsma (6) found the greatest sulphur content in the root portion and the smallest in the middle portion. He attributes variations found along the length to differences in nutrition during the periods of growth of the various portions.

Barritt and King (3) found that the sulphur content of the tip portions was generally greater than that for the rest of the fibre. They suggest that the greater sulphur content may be due to a more active sulphur-stimulus immediately after shearing. The protective action of wool grease in the denser fleeces is mentioned as a possible factor, for in two open fleeces the sulphur value for the tip portion was not appreciably higher than that for the remaining portion of the fibres.

The writers determined the sulphur content of the root, middle and tip portions of two New Zealand wools. The results are given in Table IV.

TABLE IV
VARIATION OF SULPHUR CONTENT ALONG THE FIBRE

Sample	Sulphur, %	Sample	Sulphur, %
New Zealand 36's		New Zealand 60's	
Root	3.33	Root	3.67
Centre	3.08	Centre	3.57
Tip	3.00	Tip	3.47
Original whole fibres	3.16	Original whole fibres	3.55

In both samples there is a gradation from root to tip, the root portion having the greatest sulphur content. It is reasonable to suppose that the smaller figures obtained for the tip portions are due to decomposition by exposure to light. It is true that in many cases reported the tip did not have the smallest sulphur content, but in such cases the effects can very well be explained by differences in plane of nutrition during the growth period. A better feed was probably more than sufficient to balance the loss due to the light effect. Atmospheric conditions, the amount of wax, suint, and dirt are all factors that would influence the decomposition of the wool, and it is to be expected that wide variations in the effect of light would be found.

Variation with Fineness

It has been stated at various times that fine wool contains more sulphur than coarse wool, *e.g.*, by Mullin and Hunter (13, p. 746) in reporting on the work of Takeda, and by Barker (1, p. 36). However, the evidence available is such that no definite conclusion can be reached. Some of the values quoted would indicate that the finer the wool the greater the sulphur content, but in many cases the results show no such relation. The lack in agreement is to be expected when it is remembered that fineness is not the only factor determining the sulphur content of wool. Comparison can be justified only when other conditions affecting sulphur content are equal.

Some of the evidence with respect to the relation between fineness and sulphur content will be reviewed briefly.

Barritt and King (2, p. 394), who were probably the first to carry on a fairly extensive study of the sulphur content of wool and similar fibres, quoted a value of 3.36% sulphur for the fine fibres, and 3.03% for the coarse fibres of Turkey mohair. The values given by Bonsma (6) also show, on the whole, that the smaller sulphur content corresponds to the coarser wool. A certain relation between handle and the sulphur content is also indicated by the values given. The best handling wools in general have a greater sulphur content than those with a poor handle. This has been pointed out by Sidey (15) who also investigated the relation between spinning property and sulphur content, and found that the greater sulphur content corresponded to the better spinning fibres as determined by their A/B contour ratio, in which A/B represents the ratio between major and minor axes of the elliptical cross section of the fibres.

Rimington (14) reported some results that also show coarse wool to contain less sulphur than the finer wool.

Mossini (12) has analyzed wools of various qualities and claims that his results show a direct relation between quality of the fibre and sulphur content. His figures are reproduced in Table V.

TABLE V
RESULTS OF MOSSINI

Wool	Sulphur, %
Australian AAA	3.70
Australian AA	3.28
Australian A	3.46
Buenos Ayres A/B	3.46
Buenos Ayres B	3.82
Buenos Ayres C	3.28
Buenos Ayres D	3.08
Capo AA	3.62
Capo A	3.30
Bahia A/B	3.22
Bahia B	3.31
Bahia C	3.27
Bahia D	3.74
Puglia C	2.92
Puglia D	3.26

It will be noted that the values for the Australian *A* and Buenos Ayres *A/B* qualities do not fall in the proper places if the finer qualities are to be greater in sulphur content. The Bahia finest wool has the smallest sulphur content, and the poorer quality has the greatest sulphur content of the group, while the Puglia wools are also in the wrong order. The evidence furnished by these figures is, therefore, very contradictory.

The results obtained by Winton and Edgar (17) are reproduced in Table VI in order of decreasing sulphur content. It is difficult to show any relation since the quality or fineness of the wools analyzed is not stated. However one may judge fairly closely from the breed.

TABLE VI
WINTON AND EDGAR'S RESULTS

Breed	Sulphur, %	Breed	Sulphur, %
Delaine Merino	3.76	Southdown I	3.33
Merino B type	3.63	Shropshire II	3.33
Rambouillet	3.59	Oxford	3.34
Southdown II	3.55	Columbia	3.33
Dorset	3.53	Hampshire I	3.19
Shropshire I	3.50	Romney	3.02
Hampshire II	3.49	Cotswold II	3.00
Leicester	3.45	Cotswold III	2.99
Corriedale	3.35	Lincoln	2.92
Cotswold I	3.35		

In Column 1 of Table VI the breeds are roughly in the order of decreasing fineness, the Corriedale being probably the only one out of place. In Column 3, the order is also very good except perhaps for the Oxford and Columbia samples. However, if the two columns are studied together the relation is disturbed, although the finest wools still remain at the top. It is difficult to surmise why the wools fall into two distinct groups.

Marston (11) has reported results to show that "the sulphur content of wool keratins from widely different sources were found identical within experimental error . . . .". Indeed, the total variation between the coarsest wools (Leicester and Lincoln) and the finest wool (Merino 70-74's) is only 0.07% actual sulphur. In view of the wide range of qualities covered, this difference is not significant.

Marston reported his sulphur values to the third decimal place. This is not warranted in view of the experimental error which by Marston's own statement must be of the order of 1%. The third decimal figure thus becomes meaningless, otherwise there would be a regular decrease of sulphur content as the wool becomes coarser, as his results reproduced in Table VII show.

TABLE VII
MARSTON'S RESULTS

Breed	Sulphur, %	Breed	Sulphur, %
Merino 70-74's	3.585	Polwarth 60	3.535
Merino 70	3.585	Merino 58	3.546
Merino 64	3.581	Polwarth 56	3.541
Merino 64	3.580	Shropshire 56	3.530
Merino 64	3.560	Leicester	· 3.523
Merino 60	3.562	Lincoln	3.521

Bonsma and Joubert (7) have tested a large number of samples taken from various parts of fleeces of Merino sheep of known history and maintained under definite conditions of nutrition, thereby reducing the number of variable factors. Their results show absolutely no correlation between sulphur content and fineness. It is unfortunate that similar experiments have not been carried out with other breeds, as the Merino fleeces are generally fairly uniform in quality. Table VIII, in which the wools have been grouped into classes of varying fineness, summarizes Bonsma and Joubert's results.

TABLE VIII

SUMMARY OF BONSMA AND JOUBERT'S RESULTS

Diameter range, μ	Mean % sulphur
18.0 – 18.9	3.40
19.0 – 19.9	3.34
20.0 – 20.9	3.42
21.0 – 21.9	3.35
22.0 – 22.9	3.36
23.0 – 23.9	3.44
24.0 – 24.9	3.46
25.0 – 25.9	3.44
26.0 –	3.44
Av.	3.40

The mean sulphur content for each class varies very little and may be considered constant within experimental error. How much the limitation of the tests to one breed has contributed to the constancy of the figures is difficult to say with our present knowledge.

The writers have analyzed a number of samples from various breeds. The results, given in Table IX, show no relation between fineness and sulphur content.

Nos. 1, 2, 5, 9, 10 and 11 were samples picked from sheep belonging to one experimental flock and maintained under the same conditions regarding environment and feed. Samples 2, 5 and 9 were clipped from the shoulder, while 1, 10 and 11 were samples representative of the grade chosen from the

TABLE IX

WRITERS' RESULTS FOR VARIOUS BREEDS

No.	Breed	Quality	Sulphur, %
1	Suffolk	56's (G)	3.92
2	Oxford	{ 50's (G) 44's (L)	3.85
3	Cheviot	48's (G)	3.83
4	Southdown	56's (G)	3.79
5	Suffolk	48's (L)	3.77
6	Merino	64's (L)	3.75
7	Romney	46's (G)	3.70
8	Merino	64's (L)	3.64
9	Suffolk	44's (L)	3.54
10	Leicester	40-44's (G)	3.50*
11	Hampshire	56's (G)	3.20

Mean of two samples.

fleece by the grader. Nos. 4 and 7 belonged to another flock and were also representative samples. The remaining samples belonged to isolated cases. Sample 6 was a shoulder sample, while 3 and 8 were representative samples. The quality assigned to the wool for the samples marked *(G)* is that given by the grader, while for those marked *(L)* the quality was determined from fibre diameter measurements carried out in the laboratory. In the case of Sample 2, the grader had assigned a higher quality to the fleece as a whole than that determined on the smaller sample tested. Sample 9 was made up of black and partly black fibres picked from Sample 1.

Another series of determinations was carried out on carefully sorted New Zealand wool samples picked out in one particular mill. The results obtained on these wools are given in Table X. The fineness is that given by the wool sorter.

These figures show some correlation between fineness and sulphur content in that the 44-46's wool is greater in sulphur content than the 36-40's qualities, and the 48-50, 54-58, 60, 64-70's qualities have an increasing sulphur content. However, the relation is spoiled by the discontinuity occurring between the 44-46's and the 48-50's groups. As the types of wool comprising the various qualities are not known, it is impossible to give an explanation for this break.

From all this accumulated evidence there is some indication that the sulphur content varies with fineness, but no definite relation can be enunciated. The best that can be said is that the finer wools are generally associated with a high sulphur content and the coarsest wools with a low sulphur content. If there is a relation between fineness and sulphur content, it is probably hidden in most cases by the disturbing influence of other factors, such as inheritance effects, nutritional conditions, climatic conditions. The effect of light has already been shown to be important, and it is doubtful whether concordant results can ever be obtained as long as this effect is neglected. In order to eliminate its influence, comparison on the root portions only of fibres should probably be made. In this connection microdeterminations of sulphur made on a few fibres whose diameters have been measured would be very desirable, and the combustion method would be very suitable for this purpose.

TABLE X

VARIATION OF SULPHUR WITH FINENESS

Fineness	Sulphur, %	Mean, %
36's	3.16	
38's	3.20	
40's	3.12	3.16
44's	3.35	
46's	3.43	3.39
48's	3.09	
50's	3.05	3.07
54	3.31	
56	3.33	
58	3.27	3.30
60	3.35	
64–70	3.67	

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CONTRIBUTIONS TO THE BIOCHEMISTRY OF BROMINE

II. THE BROMINE CONTENT OF HUMAN TISSUES[1]

By A. H. NEUFELD[2]

Abstract

A study of the bromine content in human tissues was made by the method outlined in Part I of this series. In many cases, total halogen determinations were made on the same material. The results suggest the following conclusions:

Bromine is a constituent of all human tissues. The amounts found in the same tissue show definite variations.

No evidence could be found to support the view that bromine is concerned with pituitary function. The thyroid contains amounts of bromine slightly greater than the amounts found in blood. While functional significance cannot be excluded, it has not been ascertained.

No definite relation was found to exist between the distribution of bromine and chlorine in human tissues.

Introduction

The work reported on in Part I of this series has been extended to the study of bromine in human tissues. The values in the literature show wide variations, largely owing to inaccuracy of the methods used. This cause of error was fully discussed in the first paper (15). Because of such inaccurate methods, theories ascribing, for example, a special function to the pituitary (24, p. 58) in bromine metabolism are deemed fallacious.

Experimental Results

In the present paper, results are given for the available tissues of five persons. Two were killed accidentally. One was a boy of 14 years, Case 1, and the other a woman of 50 years, Case 2. They were apparently in normal health at the time of death. Of the others, a man of 70 years and a man of 71 years, Cases 3 and 4 respectively, died from heart failure (cardiac myocarditis). A woman of 50 years, Case 5, died from cerebral haemorrhage. No definite lesions were found in any of the tissues examined in the last three cases.

The results obtained are given in Table I. All bromine analyses, with three exceptions, were carried out in duplicate, and agreement similar to that shown in the analyses recorded in the first paper of this series was obtained. Only the mean results, therefore, are given.

Ucko (21), in a recent paper, claimed that there is a definite relation between the bromine and chlorine contents of mammalian tissues, while Leipert (10) has claimed that such a definite ratio also exists in blood, urine and gastric juice. The writer has analyzed a large number of tissues for total halogen, using Van Slyke's method (20). The results (means of duplicate determinations) are given in Table I, expressed in terms of chlorine.

In the last column of Table I are given the equiatomic distribution ratios of bromine and chlorine in terms of chlorine. The necessary corrections for iodine have not been made, except for the thyroid material. Since the iodine contents of other tissues are extremely small, the values taken for chlorine are sufficiently accurate.

TABLE I

<small>Content of Water, Bromine, and Total Halogen (as Chlorine) in Human Tissues</small>

Tissue	Water content, %	Bromine		Total halogen (Cl)		Ratio Br/Cl × 10²	Equiatomic distribution Br/Cl × 10²
		Dry tissue, mg. %	Fresh tissue, mg. %	Dry tissue, %	Fresh tissue, %		
Case No. 1							
Adrenal	64.13	0.6	0.22	–	–	–	–
Bile (bladder)	87.05	2.7	0.35	–	–	–	–
Blood	77.10	3.35	0.765	1.089	0.249	3.07	1.50
Bone (rib)	67.83	0.85	0.275	0.362	0.116	2.37	1.05
Cerebellum	79.76	1.15	0.235	0.426	0.086	2.73	1.21
Cerebrum	77.38	0.6	0.135	–	–	–	–
Gall bladder	81.52	1.2	0.22	–	–	–	–
Heart	80.27	0.7	0.14	0.362	0.071	1.97	0.81
Large intestine	72.73	2.05	0.56	–	–	–	–
Small intestine	81.81	1.05	0.19	–	–	–	–
Kidney	77.73	1.5	0.335	0.883	0.197	1.71	0.76
Liver	76.71	0.55	0.13	0.655	0.152	0.86	0.38
Lung	81.54	1.8	0.33	–	–	–	–
Muscle	76.57	1.25	0.295	0.248	0.058	5.09	2.26
Pancreas	74.63	1.95	0.495	–	–	–	–
Prostate	82.48	1.6	0.28	–	–	–	–
Spleen	79.81	2.2	0.445	–	–	–	–
Stomach	80.47	4.3	0.84	1.323	0.258	3.26	1.45
Testes	83.97	1.6	0.255	1.340	0.215	1.19	0.53
Thymus	80.82	0.7	0.135	–	–	–	–
Thyroid	76.74	10.0	2.325	0.679	0.158	14.72	7.08
Case No. 2							
Blood	85.11	4.15	0.62	1.779	0.265	2.34	1.04
Bone (rib)	52.90	0.6	0.28	0.205	0.096	2.92	1.29
Cerebellum	78.76	0.6	0.13	0.484	0.103	1.26	0.56
Cerebrum	82.58	0.15	0.025	0.470	0.082	0.30	0.14
Heart	71.19	1.0	0.29	0.439	0.126	2.30	1.02
Small intestine	60.16	1.85	0.74	0.477	0.190	3.89	1.77
Kidney	73.46	3.1	0.82	0.926	0.246	3.33	1.48
Liver	72.96	0.15	0.04	0.389	0.105	0.38	0.17
Lung	82.45	2.65	0.465	1.450	0.254	1.83	0.81
Medulla—lower*	73.02	0.7	0.19	–	–	–	–
Medulla—upper†	70.78	0.6	0.175	0.342	0.100	1.75	0.78
Muscle	64.96	1.6	0.56	0.268	0.094	5.86	2.65
Pancreas	66.95	1.35	0.445	0.461	0.152	2.93	1.30
Pituitary	80.44	0.6	0.12	–	–	–	–
Spleen	77.47	1.0	0.225	0.616	0.139	1.62	0.72
Stomach—cardiac	73.35	2.3	0.61	0.757	0.202	3.02	1.34
Stomach—pyloric	68.55	1.7	0.535	0.509	0.160	3.34	1.49
Thyroid	77.77	8.0	1.78	0.660	0.147	12.11	5.68
Uterus	78.91	4.0	0.84	1.068	0.255	3.76	1.67

TABLE I—*Concluded*

CONTENT OF WATER, BROMINE, AND TOTAL HALOGEN (AS CHLORINE) IN HUMAN TISSUES

Tissue	Water content, %	Bromine		Total halogen (Cl)		Ratio Br/Cl × 10³	Equiatomic distribution Br/Cl × 10³
		Dry tissue, mg. %	Fresh tissue, mg. %	Dry tissue, %	Fresh tissue, %		
Case No. 3							
Blood	74.70	4.0	1.01	0.922	0.233	4.34	1.93
Heart	79.48	1.3	0.265	–	–	–	–
Liver	74.38	1.3	0.335	–	–	–	–
Lung	82.71	2.5	0.43	–	–	–	–
Spleen	76.46	1.9	0.445	–	–	–	–
Case No. 4							
Heart	78.41	1.5	0.325	–	–	–	–
Liver	77.31	1.6	0.365	–	–	–	–
Lung	79.50	3.5	0.715	–	–	–	–
Spleen	81.13	2.6	0.49	–	–	–	–
Case No. 5							
Bile (bladder)	91.71	4.0	0.33	–	–	–	–
Cerebellum	78.52	1.55	0.335	–	–	–	–
Cerebrum	77.69	0.2	0.045	–	–	–	–
Heart	78.86	0.3	0.065	–	–	–	–
Kidney	68.95	1.5	0.465	–	–	–	–
Liver	73.63	2.2	0.43	–	–	–	–
Lung	80.39	2.6	0.51	–	–	–	–
Medulla	75.00	1.1	0.275	–	–	–	–
Ovary	83.82	0.95	0.155	–	–	–	–
Pituitary	80.31	0.8	0.155	–	–	–	–
Spleen	78.44	2.7	0.58	–	–	–	–
Stomach	74.67	1.6	0.405	–	–	–	–
Uterus	80.92	1.4	0.265	–	–	–	–

*Lower half of medulla oblongata.
†Upper portion of medulla oblongata, including part of pons.

Discussion of Results

Among the values in the literature that appear to be too low, because of the use of unreliable methods (15), are those of Pribram (17) (no bromine in the brain, liver, pancreas and thyroid), Lobat (12) (no bromine in the liver, heart, spleen, kidney, blood serum; 0.015–0.02 mg. % in the cerebrum, and 0.07–3.0 mg. % in the thyroid), and Serbescu and Buttu (19) (no bromine in the liver, pancreas, heart, spleen, kidney, adrenal, pituitary, lung, muscle, and 0.415–3.15 mg. % in the thyroid). On the other hand Justus (9) analyzed 12 organs and found bromine present in each organ, the results varying from 14 to 122 mg. %; his method, undoubtedly, gave results that were too high.

Bernhardt and Ucko (1) published a long series of analyses, but, as Olszycka (16) has shown, these results are inaccurate and, therefore, cannot be considered. for comparison.

With the exception of those of blood, few analyses based upon sound methods are available in the literature. These analyses are contrasted in Table II with the writer's analyses of the same tissues. Ucko's figures are included. His new method (21) has not been checked by other writers, and it may be open to the criticism made of the method of Bernhardt and Ucko (1). It will be seem that the figures are of the same order, but show wide variations. The variations are probably, in part, due to varying bromine intake (in diet and perhaps in medication) in the cases studied.

TABLE II

BROMINE CONTENT OF FRESH HUMAN TISSUES (VARIOUS WRITERS)

Tissue	Damiens (3)	Dixon (4)	Ucko (21)	Neufeld
	Mg. per 100 gm.			
Adrenal	–	–	0.33–0.66	0.22
Blood	0.52	0.28–1.64	0.15–0.35	0.62 –1.01
Kidney	0.25	–	0.27	0.335–0.82
Liver	0.18–0.37	–	0.17	0.04 –0.43
Lung	0.14–0.28	–	–	0.33 –0.715
Pituitary	–	0.42–2.39	–	0.12 –0.155
Spleen	–	–	0.24–0.33	0.225–0.58
Thyroid	–	–	0.48	1.78 –2.325

Bromine in blood. In addition to the figures recorded in Table II, the following apparently reliable values (in mg. %) have been published for individuals presumed normal, and not known to have been given bromine compounds therapeutically: Quastel and Yates (3 cases), 0.83–1.46 (18); Guillaumin and Merejkowsky (8 cases), 0.74–1.60 (6); Leipert (10 cases), 0.16–0.4 (10); and Ucko (100 cases), 0.15–0.35 (21).

Concerning the distribution of bromine between the corpuscles and plasma, Guillaumin and Merejkowsky (6) found the ratio "corpuscle Br to plasma Br" higher than the corresponding ratio for chlorine, while Hastings, Harkins and Liu (8) obtained a smaller value. Hastings and Van Dyke (7), and Leipert (10) found that normally there is a slight retention of bromine in the corpuscles, in agreement with the views of Böniger (2) on the permeability of the bromide ion. The bromide distribution between cells and plasma is not a constant value, but is dependent on the carbon dioxide content of blood, similar to chloride (Hastings and Van Dyke (7), and Leipert (10)).

Guillaumin and Merejkowsky (6) stated that 63 to 88% of the bromine is in organic combination; Ewer (5) found 55 to 78%; while Ucko (21) found only 20% of blood bromine in organic combination (he states that it is not in combination with plasma proteins). On the other hand, Yates ,(23) states

that all bromine in blood is in inorganic form. This latter work has been verified by Leipert (10) by means of deproteinization, dialysis and ultra-filtration, and this conclusion is almost certainly correct; the findings of Guillaumin and Merejkowsky, Ewer and Ucko must be rejected.

The results reported in this paper for normal blood are 0.62 to 1.01 mg. % (3 cases). The variation in bromine content is probably due mainly to differences in bromine intake.

Bromine in cerebrospinal fluid. The chlorine content of cerebrospinal fluid is always higher than that of blood plasma, in accordance with the Donnan equilibrium. Mishkis, Ritchie and Hastings (13) found that the concentration of bromine in the cerebrospinal fluid is always lower than the corresponding concentration in blood plasma. After the administration of bromide, Walter (22) observed a similar distribution. He found the ratio of "plasma Br to cerebrospinal fluid Br" normally to be 2.9–3.3. Leipert and Watzlawek (11) have obtained similar results, although they point out that this rather indicates a difference of permeability to anions, and not to bromide in particular.

Bromine in gastric juice. Nencki and Schoumov-Simanovsky (14) were the first to show that when bromide is administered it replaces part of the chloride in the gastric juice. Quastel and Yates (18) found a drop of 25 to 30% of bromine in the blood following a meal. Leipert (10) has obtained similar results. The actual contents of gastric juice in his four analyses were 0.312 to 1.226 mg. %, each one higher than the corresponding blood bromine. Ucko (21) found the value to be 0.5 to 0.9 mg. per 100 cc. in gastric juice from the "fasting" stomach.

Bromine in urine. The excretion of bromine in urine in absence of specified bromine administration has been determined by a number of writers. Leipert (10) found this value to be 3 to 5 mg. per 24 hr., and Ucko (21), 1.0 to 2.5 mg. Both writers and also Hastings, Harkins and Liu (8) state that the ratio "bromine to chlorine" is always slightly lower in urine than in blood.

Bromine in the pituitary. The assumption that the function of the pituitary is important in bromine metabolism, as set out by a number of writers (reviewed in Part I of this series), has not received any confirmation in the more accurate work of Dixon (4). The results obtained by the writer (in Parts I and II of this series) are in full agreement with those of Dixon.

Bromine in the thyroid. In the first paper of this series the results appeared to indicate that the thyroid stored amounts of bromine definitely greater than could be ascribed to blood circulating through the different tissues. Results in this paper also appear to suggest that this is the case. In addition the writer analyzed certain thyroid material obtained from the operating theatre at partial thyroidectomy. The results obtained for bromine, iodine, and total halogen are shown in Table III in mg. %. All the operative cases had been treated with Lugol's solution prior to operation.

TABLE III

ANALYSES OF HUMAN THYROID MATERIAL (mg. %)

	Water	Bromine		Iodine		Total halogen		Equiatomic distribution
		Dry tissue	Fresh tissue	Dry tissue	Fresh tissue	Dry tissue	Fresh tissue	Br : I : Cl
Normal	76.74	10.1	2.33	169.0	39.3	678.5	157.8	1 : 10.6 : 141.2
Normal	77.77	8.1	1.78	107.0	23.8	660.0	146.8	1 : 8.4 : 176.2
Graves' disease	81.94	50.3	9.08	264.5	47.8	752.5	135.9	1 : 3.3 : 29.5
Graves' disease	86.30	12.45	1.71	186.5	25.6	760.5	104.2	1 : 9.6 : 127.0
Graves' disease long standing	87.97	6.8	0.82	83.0	10.0	597.0	71 8	1 : 8.0 : 188.6
Pressure symptoms non-toxic goitre	82.58	13.05	2.28	43.5	7.6	4157.0	724.0	1 : 2.1 : 713.2

The results in Table III show variations in the ratios of the three halogens that are too great to permit any conclusions to be drawn beyond the fact that in the thyroid the ratio of bromine to chlorine is greater than that in other tissues. This, perhaps, supports the view that bromine is concerned with thyroid metabolism, although the writer (15) could find no evidence that bromine is associated with the functioning compound, thyroglobulin, of the thyroid. Nevertheless, all the findings recorded in this and in the previous paper suggest that a more detailed study of thyroid material may reveal some functional significance for bromine in this gland; it is hoped to carry out such a study at a later date.

Bromine to chlorine ratio. Earlier figures for human and other mammalian tissues (weight-ratios) are summarized and given in Table IV (all $\times$ 10³).

TABLE IV

THE BROMINE TO CHLORINE RATIO IN MAMMALIAN TISSUES

	Ucko (21)	Leipert (10)	Damiens (3)	Neufeld
Organs (not including thyroid)	1.5-8.0	–	0.21-4.53	1.19-5.86
Gastric juice	1.7-5.5	1.54-3.98	–	–
Blood	0.5-1.4	0.62-1.42	1.32-1.55	2.34-4.34
Urine	0.3-0.6	0.41-0.57	0.39-1.85	–

These figures, and the detailed figures in Table I do not show sufficient constancy to suggest that any physiological ratio exists. The figures in Table I suggest that the ratio for the thyroid is relatively much greater than for other tissues, but these are based on only two analyses, while Ucko (21) did not, in his analyses, find such high ratios. This finding, therefore, cannot be stressed until a larger number of analyses have been made.

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STUDIES OF CARBON BLACK

III. THE CHANNEL PROCESS—PRODUCTION FROM PYROLYSIS WASTE GASES[1]

By L. M. PIDGEON[2]

Abstract

The waste gases obtained during the pyrolysis, in baffled metal tubes, of 70:30 propane-butane mixtures at temperatures between 800° and 850° C., with the object of producing liquid aromatics, have been used to produce carbon black in an experimental channel plant. The hydrocarbon mixture if utilized directly to produce carbon black yielded up to 4.9 lb. per 1,000 cu. ft. When the mixture was subjected to pyrolysis about 33 lb. of liquids (23 lb. in the gasoline range) was produced, while the off-gas yielded 5.4 lb. of carbon black. Yields of carbon black up to 10 lb. per 1000 cu. ft. were obtained with lower yields of liquid. Experiments on synthetic gas mixtures showed that the olefines were largely responsible for the production of carbon black from the pyrolysis off-gas. A large number of tests on rubber indicated that the carbon reinforces rubber in a manner as good as or better than that of the commercial gas blacks at present used in the rubber industry.

Introduction

The channel process, which is employed almost exclusively in the production from natural gas of the carbon black used largely in the rubber industry, is so wasteful that it fails to recover more than a small fraction of the carbon present in the gas. The carbon black industry depends, therefore, on the existence of enormous amounts of hydrocarbon gases for which no other use can be found and which otherwise would be wasted after removal of the natural gasoline. So large, however, have been the amounts of gas available for carbon black production that supply has exceeded demand in recent years, a condition that has been responsible for the low price to which carbon black has fallen. In these circumstances it may be readily understood that little incentive has been offered to improve the methods of production. This situation, while it will undoubtedly continue for some time, cannot be regarded as a permanent one, and indications of a change are already in view. Eventually more economical methods of production must be evolved, or the price of carbon black will increase, and a readjustment of the relative position of this filler in the rubber industry must take place.

Thermal process methods have achieved notable improvements in the carbon recovery but, to date, they have been unable to duplicate the quality of channel blacks and have, therefore, enjoyed but limited application. It seems that initial attempts to improve the methods of production might well

take the form of more efficient utilization of the gas supplies on hand, by the use of the established flame impingement process.

In the experiments to be described it has been found that the off-gas from low-pressure pyrolysis carried out on propane and similar gases in the Cambron Bayley apparatus*, with the object of securing liquids (mostly aromatic) as the primary product, is eminently suitable for the production of carbon black by the channel process. In fact, the amount of black that may be produced from a given volume of stabilizer gas is considerably greater if the gas is first caused by pyrolysis to yield aromatic liquids and the off-gas is then burned, than if the stabilizer gas is burned directly.

The gases that have been employed in these experiments were produced during the pyrolysis of a mixture of propane and butane, this particular mixture being employed because of its similarity to stabilizer gas of which large amounts are available in various parts of the world. The pyrolysis of these gases was carried out by Cambron and Bayley, who have described the experimental details (1, 2, 3, 4). The hydrocarbon mixture was passed through metal tubes at temperatures up to 850° C., the tubes being equipped with a special system of baffles designed to produce turbulent flow and thereby assist the process of heat exchange. These authors placed the off-gas at the disposal of the writer.

The composition of the gas obtained from the pyrolysis of a hydrocarbon mixture depends on the conditions of operation. The initial step in pyrolysis is the formation of olefines, while further heating results in the "polymerization" of these gases to aromatics and other hydrocarbons, depending on the temperature and pressure at which the operation is carried out. The highest yields of carbon black would be expected from the off-gas when its olefine content is a maximum, since it is well known that gases containing large amounts of "illuminants" are prolific producers of carbon in free flames. The conversion of olefines to aromatics involves an increase in the percentage of methane and hydrogen and a reduction in the carbon content of the off-gas, which consequently reduces the yield of carbon black which may be obtained. It has been noticed, however, that the ethylene concentration does not fall below a certain value unless the pressure at which the pyrolysis operation is carried out is materially increased. When the time of contact in the pyrolysis process is lengthened and the yield of aromatics thus increased, a larger volume of off-gas is produced. This gas expansion may be such that, despite the fact that the off-gas is "leaner", the total yield of carbon black is not seriously reduced.

The effect on the yield of carbon black of varying the gas composition has been examined both by altering the conditions in the pyrolysis, so as to produce off-gas of various compositions, and by the use of synthetic mixtures. In order to ascertain the relative efficiency of the joint pyrolysis-channel process, a number of determinations have also been made on the possibilities of carbon black production from the original propane-butane mixture, without preliminary treatment in the pyrolysis apparatus.

* *U.S. Patents 2,002,524 and 2,002,525; also patents elsewhere. Cf. references 1–4.*

Experimental

PRODUCTION OF CARBON BLACK

Apparatus and Method

The production of carbon black was carried out in the experimental channel plant which has been described in detail (11). The 6 in. channel employed in the previous experiments was replaced by an 8 in. channel, but otherwise the conditions were identical with those already described.

The gases passed from the charcoal absorbers of the pyrolysis apparatus to a gasholder of 4 cu. ft. capacity, and thence to the channel plant. The conditions of operation of the pyrolysis apparatus were similar to those of Cambron and Bayley's experiments Nos. 65–69 (4), with the exception that a 70:30 propane-butane mixture was employed in place of propane. This substitution resulted in a slight enrichment of the off-gas, chiefly represented by higher olefine concentrations, but did not change the general relations in any way.

It has been indicated (11) that when the gas composition, the gas pressure, and the burner tip have been specified in a given experimental apparatus, the important remaining variables are channel height and draft control. Many other factors exist that might presumably influence the results, but experience has shown that they exert only a small effect, although quantitative information on the subject is not available. Attention has, therefore, been confined to the effect of channel height, draft control, and gas composition on the yield and characteristics of the carbon black.

Effect of Channel Height

The effect of channel height has been examined by the use of a very rich gas that happened to be available in large quantities during a life test performed on the metal tubes of the pyrolysis furnace. No liquids were formed during the pyrolysis, so that this gas is a suitable one for the recovery of the

TABLE I

EFFECT OF CHANNEL HEIGHT ON YIELD

Experiment	A Carbon collected from walls and channels				B Carbon from channels					
	C11	C10	C12	C13	C29	C16	C17	C18	C19	C21
Channel height, in.	1.84	2.24	2.56	3.24	1.92	2.94	2.44	2.84	3.20	3.61
Yield, lb. per 1000 cu. ft.	4.2	4.7	4.8	4.6	3.3	4.1	4.4	3.9	3.4	2.2
Yield based on propane-butane pyrolyzed	8.4	9.4	9.6	9.2	6.6	8.2	8.8	7.8	6.8	4.4

Gas composition: C_2H_4, 24.0; C_3H_6, 12.3; C_2H_2, 1.3; H_2, 14.8%; *paraffin residue, 47.6%.*
Expansion, 100%.
Burner: Cabot type, 0.022 in. slot. Gas rate, 6 cu. ft. per hr. Drafts, 28%.

ı ıximum amount of carbon black. The results are shown in Table I and plotted in Fig. 1. For a given channel height, a sharp maximum is obtained, the position of which depends on the particular tip and gas pressure chosen.

The yields obtainable from this gas are at least three times as great as those produced from methane. They also represent a considerably higher percentage of the theoretical recovery of the carbon, as will be seen presently.
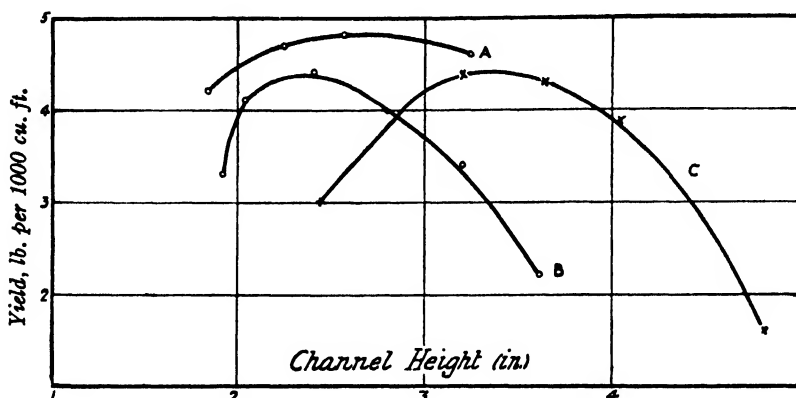
Fig. 1. *Effect of channel distance on yield (0.022 in. Cabot tip). A. Pyrolysis off-gas, all carbon in burner chamber recovered. B. Pyrolysis off-gas, carbon from channels only. C. Propane-butane, carbon from channels only.*

Table II shows the yields obtained with the original propane-butane mixture. Again a fairly sharp maximum channel setting is required to obtain the optimum yield. In the yields obtained from the rich waste gas, to determine the actual recovery from the propane-butane pyrolyzed, the yield from

TABLE II

EFFECT OF CHANNEL HEIGHT ON YIELD

	A Burner: Cabot type, 0.022 in. slot Gas rate, 3.4 cu. ft. per hr. Drafts, 28%						B Burner: Cabot type, 0.012 in. slot Gas rate, 2.22 cu. ft. per hr. Drafts, 28%						
Experiment	C31	C32	C33	C34	C45	C46	C35	C36	C37	C38	C41	C39	C40
Channel height, in.	2.44	2.84	3.20	3.64	4.04	4.84	1.24	1.64	2.04	2.44	2.84	3.24	3.64
Yield, lb. per 1000 cu. ft.	3.0	3.9	4.4	4.3	3.9	1.8	2.3	2.8	3.6	4.9	3.8	2.2	1.1

Gas composition: C_3H_6, *70;* C_4H_8, *30%.*

the waste gas must be multiplied by the expansion taking place during pyrolysis, which in this case was the factor 2. This procedure has been followed in Table I, where values as high as 9 lb. per 1000 cu. ft. are given. Thus the total yield in the joint process is considerably greater than that when the paraffins are utilized directly.

It is also evident from Table I (*A* and *B*) that, under these experimental conditions, much larger amounts of carbon are liberated from the flame than are retained on the channel. Carbon was deposited on the walls and flues of the apparatus, while considerable quantities were lost into the air. When all the carbon in the apparatus was collected, the apparent yield was much greater, as is shown in Table I, *A*, and the effect of channel height was much less pronounced, as might be expected.

Considerable doubt has been expressed as to the quality of the carbon which escapes from the flame without being deposited on the channel (12), since its genesis is similar to that of lampblack, a material that is inferior to carbon black as a reinforcing agent for rubber. In computing the yields and in subsequent tests, only carbon deposited on the channel has been considered. It would be necessary to employ a much larger depositing area than is customary in the case of natural gases composed largely of methane, if gases that burn with very smoky flames were used in full-scale practice. The same effect could be produced with smaller flames, although changes in flame dimension cannot be made without consideration of the type of carbon that it is desired to produce. The use of smaller tips increased the yield obtainable with propane-butane as shown in Table II, *B*, while with the same pyrolysis waste gas as employed in the experiments of Table I even more noticeable gains were achieved by the use of smaller burners. Thus, with a 0.012 in. tip burning gas at the rate of 3 cu. ft. per hr. the yield rose to 5.7 lb. per 1000 cu. ft., which is an improvement of 25% over the best yield given in Table I,*B*, while the amount of carbon deposited on the walls was correspondingly reduced, an effect undoubtedly desirable where continuous operations are involved, as otherwise the outlets would require constant cleaning.

Effect of Draft Control

In the previous experiments (11) in which methane was examined, it was found that when the flames burned steadily, without flicker or pulsation, no change in yield was brought about by restriction of draft, until the limit tolerated by the flames was reached, at which point the yield was seriously reduced. On the other hand, when the convection currents set up were such as to cause disturbance of the flames when the draft was unrestricted, it was found that the yield was unfavorably affected, and improvement could be achieved by restriction of draft.

A similar behavior has been observed in the present case. The results of experiments in which the same gas as that indicated in Table I was used are shown in Table III. The flames flickered badly with unrestricted draft and the yield was adversely affected. Improvement in the burning of the flames was accompanied by increase of yield as the draft was restricted, until the limit of tolerance was attained, at which point the luminosity of the flames was impaired with consequent reduction in yield. These results are in agreement with those previously given (11) and also with the opinions of Francis (7), who has indicated that theoretically no improvement in yield can follow dilution with nitrogen or carbon dioxide of the air surrounding the hydrocarbon flame.

TABLE III
Effect of Draft Control

Experiment	C22	C23	C24	C18	C25
Yield, lb. per 1000 cu. ft.	3.1	3.2	3.5	3.9	3.5
Draft aperture, %	100.0	50.0	38.0	28.0	21.0
Flue gas composition, %					
Carbon dioxide	1.0	1.5	1.8	3.8	3.5
Oxygen	19.2	17.2	16.3	14.5	14.1
Residue	79.8	81.3	81.9	81.7	82.4

Burner: Cabot type, 0.022 in. slot.   Gas rate, 6 cu. ft. per hr.   Channel height, 2.84 in.

The flue gas analyses bear no relation to those determined previously for methane (11), and show again the futility of attempting to specify draft conditions in any manner that may have general application.

As pointed out previously (11), the effect of draft control will depend on the channel height, and in exceptional circumstances very marked effects might be observed. Owing to the fact that a hydrocarbon flame becomes taller when the supply of air is restricted, the relative height of the depositing surface is altered. Thus if the channel had been set just above the flames, the recovery of carbon would be zero, while, by suitable reduction of draft, the flame might be lengthened to reach the channel upon which some carbon would then be deposited. In such circumstances draft control would obviously exert a very marked effect on the yield. The case is exceptional and in ordinary use it seems clear that the chief effect of draft control is to steady the flames.

Effect of Gas Composition

Clearly, in view of the present price of carbon black, it would not be commercially feasible to subject paraffin hydrocarbon gas to pyrolysis prior to burning it for carbon black production, if carbon black is the sole product made. If, however, pyrolysis is conducted in such a way as to yield substantially a maximum or optimum amount of aromatics, and these are collected and utilized as a source of motor fuel (of high octane rating), styrene, naphthalene, etc. (4), and the off-gas, containing olefines well suited to the production of carbon black in good yield, is then used for carbon black production, there are prospects of commercially successful operation. With this in mind a series of experiments was carried out in which the pyrolysis of a 70:30 propane-butane mixture (representing stabilizer gas) was conducted under conditions designed to yield various amounts of aromatics, and the off-gas was burned to yield carbon black by the channel process. The results are given in Table IV.

The yield of carbon black based on the off-gas decreases in a fairly regular manner as the amount of liquid products obtained during the pyrolysis increases. When, however, this yield is based on the amount of gas entering

TABLE IV

RELATION BETWEEN COMPOSITION OF OFF-GAS AND YIELD OF CARBON BLACK

Experiment	B6	B25	B12	B16	B30
Pyrolysis					
Temperature	810(s)	830(s)	810	830	850
Liquids (1 hr.), gm.	—	41.6	53.2	76.0	101.5
Expansion, %	73	99	101	103	117
Off-gas composition					
C_2H_2	0 9	0.9	1.0	0.9	1.1
C_2H_4	24.6	26.6	26.7	28.0	25.9
C_3H_6	12.0	9.5	7.5	4.3	3.1
H_2	16.3	16.7	16.6	17.7	19.7
Residue	46.2	46.3	48.2	49.1	50.2
n, Residue (C_nH_{2n+2})	1.4	1.2	1.1	1.1	1.0
Carbon black production					
Yield from off-gas, lb. per 1000 cu. ft.	3.9	3.5	3.4	2.7	2.5
Yield based on original propane-butane volume	6.6	6.9	6.8	5.5	5.4
Theoretical recovery based on off-gas, %	7.6	8.2	8.4	7.1	7.2
Theoretical recovery based on original propane-butane, %	5.9	6.2	6.1	4.9	4.8

(s)—Shorter furnace, 85 cm.

the pyrolysis apparatus, the results are somewhat different. In B6, for example, the amount of cracking was incomplete, as shown by the high propylene content and the high carbon number of the residue; hence the expansion was not great and the total yield of carbon black was less than that in B25, in which, with a lower olefine content and lower yield based on off-gas, the greater expansion has resulted in a larger over-all yield. Even when the maximum amounts of liquids are being synthesized in the pyrolysis operation, the total yield remains at a reasonable value. Thus, comparing the results of B30 and B12, the yield of liquids has been increased by 100%, while the total yield of carbon black has suffered a loss of but 18%. This phenomenon is due to the fact that in these pyrolysis experiments the percentage of ethylene remained substantially constant, even with very different yields of liquid. The increase of liquids has taken place at the expense of the amount of propylene, which decreases to less than one-half of the amount present when the yield of liquids is low.

The conditions most suitable for the production of useful aromatics are typified by Experiment B16, since, at the temperature and time of contact in question, the ratio of light oil to tar in the recovered liquids is most favorable.

The important feature of the process is the production of useful aromatic liquids in good yields without, at the same time, reducing the amount of carbon black that may be recovered from the gas. In fact the amounts of carbon black that were produced from a given volume of stabilizer gas when first pyrolyzed and burned to produce carbon black were larger than when the gas was burned directly to form carbon. Thus, the best yield obtained with the untreated paraffin mixture was 4.9 lb. per 1000 cu. ft., while the same gas, after treatment in the pyrolysis plant produced 5.4 lb. per 1000 cu. ft., and some 23 to 25 lb. of light oil per 1000 cu. ft. would be recovered during the pyrolysis. For details of the composition of this oil and of the additional 10 lb. of tar which is obtained concurrently, reference should be made to the work of Cambron and Bayley (4).

Examination of Synthetic Mixtures

Hydrogen, ethylene, and methane constitute 95% of the off-gases. These gases have been mixed in various proportions in order that a search might be made for the important factors influencing carbon yield. To reduce the number of experiments, the channel and draft settings have been kept constant. This procedure introduces some error, since the optimum conditions for a given flame may not be the same as for another. The difference, however, is unlikely to be large when flames of similar type are used.

As shown in Table V, the yield obtained from either ethylene or methane is reduced by any addition of hydrogen. There is considerable difference in the relative sensitivity of various gases to this treatment. This is clearly shown in Fig. 2, in which the yields of various dilutions with hydrogen have been plotted as a percentage of the yield obtained with the pure hydrocarbon. In the case of methane the yield is sharply reduced by small additions of hydrogen; ethylene, on the other hand, is

TABLE V

EFFECT ON YIELD OF DILUTION WITH HYDROGEN

A. Methane

CH_4	H_2	Yield, lb. per 1000 cu. ft.	Per cent of original yield
100	0	1.2	100
95	5	1.1	92
90	10	0.8	66

B. Ethylene

C_2H_4	H_2		
100	0	4.3	100
95	5	4.2	98
90	10	4.1	95
85	15	3.4	79
75	25	2.2	51

C. 25% Ethylene and methane

C_2H_4	CH_4	H_2		
25	75	0	2.2	100
25	65	10	2.2	100
25	60	15	2.1	96
25	55	20	1.9	86
25	50	25	1.8	82

Burner: Cabot type, 0.012 in. slot. Gas rate, 2.7 cu. ft. per hr. Drafts, 21%.

much less affected; while replacement of methane by hydrogen in a mixture of methane and ethylene may be carried to considerable lengths before appreciable reduction in yield takes place. This fact is of importance in the
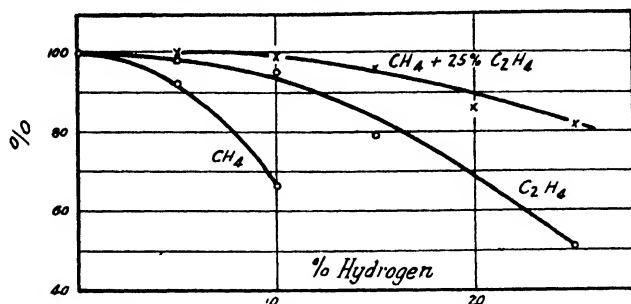
FIG. 2. *Effect on yield of addition of hydrogen to various gases.*

production of carbon from pyrolysis off-gas, as increase in the yield of aromatics by pyrolysis tends to increase the proportion of hydrogen in the off-gas. In mixtures of this type the major portion of the carbon is supplied by the olefines, and, as long as the diluent gas is inflammable so that its presence does not seriously reduce the flame temperature, considerable amounts of the latter may be present before the yield is appreciably reduced. An example of this phenomenon is found in some results of Wiegand (14), who reported yields similar to those obtained with methane (1.0 to 1.3 lb. per 1000 cu. ft.), using a gas of the following composition:— H_2, 36.0; CO, 26.4; CH_4, 16.4; CO_2 and N_2, 13.2; illuminants, 7.2; O_2, 0.8%. With such a gas almost the whole recovery of carbon black must be due to the olefines.

The value of ethylene as a source of carbon black is further shown by the data in Table VI, where it can be seen that the yield varies with the amount of olefine added.

TABLE VI

EFFECT OF ADDITION OF ETHYLENE

Methane

CH_4	C_2H_4	Yield, lb. per 1000 cu. ft.
100	0	1.2
95	5	1.4
90	10	1.7
75	25	2.2
60	40	2.7

10% Hydrogen and methane

H_2	CH_4	C_2H_4	
10	90	0	0.8
10	85	5	1.3
10	80	10	1.6
10	65	25	2.2

A general summary of these results and those obtained with pyrolysis off-gas is given in Table VII. The higher yields obtained with the off-gas is due entirely to the presence of propylene as shown in Fig. 3. Extrapolation of the curve relating yield to propylene concentration gives a yield (2.0 lb. per 1000 cu. ft.) almost identical with that obtainable with synthetic mixtures containing the same ethylene concentrations. Hence, from these values it is possible to forecast, with a reasonable degree of certainty, the yields that would be obtained from any given mixture of gases.
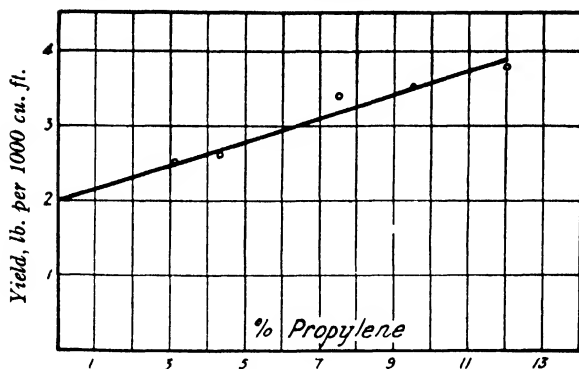
FIG. 3.   *Relation between propylene concentration in pyrolysis waste gas and carbon black recovery.*

TABLE VII

RELATION BETWEEN GAS COMPOSITION AND YIELD OF CARBON BLACK

	Pyrolysis off-gas					Synthetic gas	
C_2H_2	0.9	0.9	1.0	0.9	1.1	0.0	0.0
C_2H_4	24.6	26.6	26.7	28.0	25.9	25.0	25.0
C_3H_6	12.0	9.5	7.5	4.3	3.1	0.0	0.0
H_2	16.3	16.7	16.6	17.7	19.7	10.0	20.0
Residue	46.3	46.3	48.2	49.1	50.9	65.0	55.0
Yield, lb. per 1000 cu ft.	3.8	3.5	3.4	2.7	2.5	2.1	1.9

PHYSICAL PROPERTIES OF CARBON BLACK FROM PYROLYSIS WASTE GASES

Owing to the lack of a test capable of satisfactorily evaluating the properties of a carbon black designed for use in rubber, it is necessary to compare the new samples with standard commercial samples such as are in common use in the rubber industry.   In appearance the experimental blacks had all the characteristics of typical channel blacks, showing the same intense black and high tinting strength.   Grit was practically absent and the ash content was very nearly zero, owing to the smooth face of the depositing surface and the efficiency of the scrapers.   The samples could be brushed through the finest screen without any residue being left.

The sorption of methylene blue was examined under experimental conditions similar to those described previously (10).   The value for a sample obtained under conditions productive of maximum yield is shown in Table VIII, together with values obtained with commercial blacks under similar conditions.

TABLE VIII

SORPTION OF METHYLENE BLUE*

Sample	Mg. per gm. of carbon
Pyrolysis off-gas	37.6
Standard rubber black *B*	33.6
Standard rubber black *A*	32.0

* *0.25 gm. black shaken for one hour with 50 cc. of 0.25% aqueous methylene blue solution.*

The carbon obtained from the pyrolysis off-gas showed slightly greater sorptive capacity under this test, but, as will be shown presently, the rate of vulcanization was actually more rapid than that with the commercial sample.

Reinforcement of Rubber

A preliminary examination was made by the use of the D.P.G. test formula, which has been described by the writer (11). The tensile properties of a sample produced from pyrolysis waste gas under conditions of maximum yield are shown in Table IX. The particular commercial sample, which was examined under identical conditions, gave somewhat lower values as shown.

TABLE IX
RUBBER REINFORCEMENT BY CARBON BLACK

Cure time, min.	200 %	300 %	400 %	500 %	T_b	E_b, %	Hardness (Shore)
C18							
65	35.5	70.4	111	181	220	565	57
85	52.1	101	162	237	282	560	64
105	56.6	106	174	252	287	555	64
125	63.2	111	179	257	282	530	64
Standard rubber black—Manufacturer "A"							
65	28.7	58.2	98.6	153.4	233	630	56
85	37.4	73.7	123.0	188	270	610	59
105	40.8	79.1	131.4	196	279	618	61
125	47.1	87.3	142.6	211	278	590	63

	Abrasion loss, cc. per hp-hr.
C18 *	151
· Standard Rubber Black "A" *	161

* *Cure time 95% of the optimum as shown by tensile tests. Stress, kg. per sq. cm.*

Results of abrasion tests, obtained with the du Pont abrader by the use of the procedure recommended by the makers of this apparatus, are given in Table IX. The new black is slightly superior to this particular commercial sample.

Effect of Loading on Tensile Properties

Wiegand (14) has emphasized the importance in the evaluation of reinforcing agents of the energy or "proof resilience", which is essentially the work done in stretching the sample to the breaking point. When the energy for different pigment loadings is compared with that of the base mix, it is possible to obtain a curve that is representative of reinforcement and that exhibits a characteristic shape for any given filler. Wiegand suggests the

name "delta A" (ΔA) for this function, which is simply the double integral of tensile strength with respect to the elongation and percentage of pigment in excess of the base mix.

The evaluation of the ΔA function is likely to afford a clearer picture of the relative reinforcing properties of two pigments than that obtainable from a single determination using the same loading and accelerator.

To obtain results that will be comparative, it is necessary to choose an accelerator the effectiveness of which is relatively independent of the concentration of pigment. If this precaution is neglected, the results will be meaningless, and, as pointed out by Cranor and Braendle (5), attempts to adjust the differences in cure time by changing the concentration of accelerator will result in the introduction of enormous errors. These authors employed a heavily loaded litharge mix which was found to be nearly independent of the pigment concentration. In the present investigation the accelerator, Captax (mercaptobenzo-thiazole) was found to be satisfactory, since only small differences in rate of cure were noted with various concentrations of carbon black. The following formula has, therefore, been employed: Smoked sheet, 100; zinc oxide, 5; stearic acid, 4; Agerite resin, 1; Captax, 1; sulphur, 3; Genasco, 5.

Carbon black was added to the various mixes in the following proportions by weight (rubber 100), *viz.*, 15, 35, 55, 75, and 100. The accelerator was added from a master batch and the sulphur was added last to the mix in order to reduce the danger of scorching, and also in deference to a suggestion appearing in the literature (9) that flocculation of the carbon may take place around the sulphur particles when they are present during the addition of the carbon. Vulcanization and testing were carried out as described previously, cures being made at 274° F. for 30, 45, 60 and 75 min. respectively.

The tensile results obtained in these experiments are shown in Table X and in Figs. 4 and 5, where the ultimate tensile strengths have been plotted against the time of cure. It is evident that this accelerator is relatively independent of the concentration of the carbon. At low loadings a slight retardation of cure is observed, while at the highest loadings a slight acceleration appears, although the curves at these concentrations are very flat. These differences are in the same direction as, but much smaller than, those observed by Goodwin and Park (8), using this accelerator with commercial blacks.

The behavior of the new carbon black in rubber is almost identical with that of the standard commercial sample, such differences as appear being no greater than would be found between two commercial samples obtained from different producers. The most noticeable difference is the greater stiffness that is imparted by a given concentration of the new black. This excessive stiffness proves to be detrimental at the highest loadings as the ultimate elongation and tensile strength are reduced. On the other hand, the new black will give the same stiffness and tensile strength at lower carbon loadings.

TABLE X

TENSILE PROPERTIES AT VARIOUS LOADINGS

Cure, min. at 274° F.	Carbon black from pyrolysis off-gas					Standard carbon black *B*				
	300 %	500 %	T_b	E_b, %	Hardness (Shore)	300 %	500 %	T_b	E_b, %	Hardness (Shore)
Base stock										
30	17.2	51.0	215	740	40					
45	20.6	60.0	228	718	42					
60	22.5	67.2	241	683	43					
75	22.5	67.6	222	690	44					
15 parts carbon										
30	21.9	64.8	196	740	44	19.9	62.4	173	715	43
45	27.7	82.1	240	737	47	27.2	84.1	224	703	47
60	33.8	100	272	738	49	32.1	100	252	697	49
75	37.5	109	277	720	51	36.1	110	283	713	50
35 parts carbon										
30	41.3	110	188	655	54	33.6	94.7	162	648	51
45	58.8	147	274	705	58	49.4	134	264	713	56
60	68.5	170	288	676	61	62.6	162	284	680	59
75	73.7	178	285	665	63	66.0	172	279	663	61
55 parts carbon										
30	73.4	162	208	598	63	59.6	141	190	603	66
45	97.6	205	251	591	69	84.1	189	265	645	68
60	112	231	270	588	71	100	218	280	613	70
75	124	246	272	553	73	110	234	284	598	71
75 parts carbon										
30	135	222	229	500	76	101	201	215	540	70
45	161	–	248	480	81	136	238	251	535	76
65	182	–	248	428	82	153	253	255	503	79
75	195	–	247	395	83	161	–	259	478	81
100 parts carbon										
30	192	–	215	350	84	171	–	211	410	84
45	216	–	216	300	88	194	–	226	383	86
65	–	–	220	265	90	218	–	239	345	87
75	–	–	217	238	90	224	–	236	328	90

Stress, kg. per sq. cm. (Hardness—Shore "Durometer")

Smoked sheet, 100; zinc oxide, 5; stearic acid, 4; Agerite resin, 1; Captax, 1; sulphur, 3; Genasco, 5.
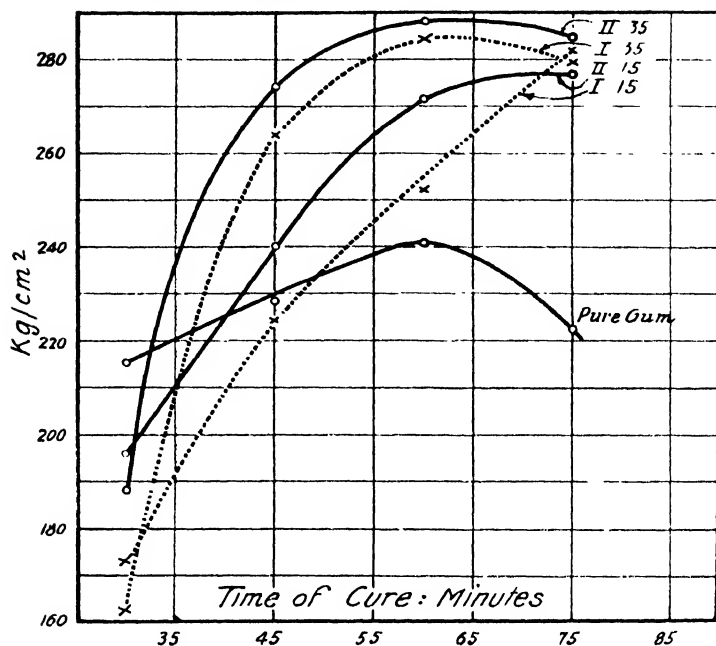
FIG. 4.   *Ultimate tensile strength at various cure times.   I. Standard rubber black B.*
II. Carbon black from pyrolysis off-gas.
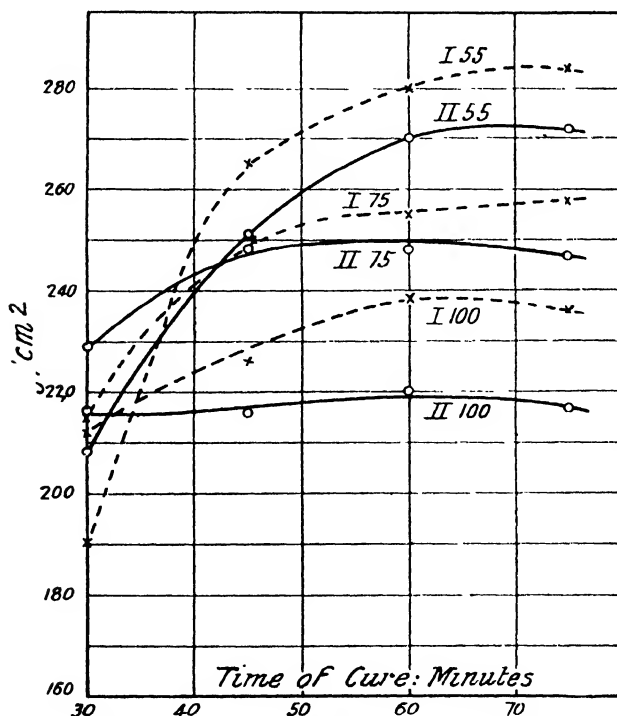
FIG. 5.   *Tensile properties at various cure times.   I. Standard rubber black B. II. Carbon*
black from pyrolysis off-gas.

Delta-A Function

The stress-strain curves corresponding to the results of Table X were plotted and the areas under the curves obtained by means of a planimeter. These values, which correspond to the energy required to break the samples, are plotted against the concentration of carbon black in Fig. 6. Further
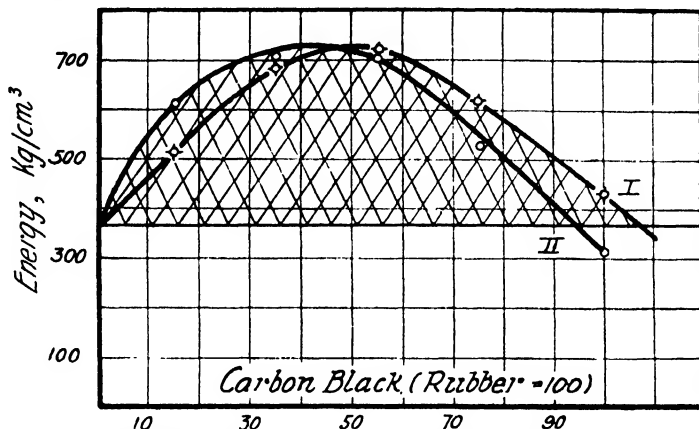
FIG. 6.   Energy-concentration relation.   I. Standard rubber black B.   II. Carbon black from pyrolysis off-gas.

evidence of the fundamental identity of these two carbons is shown by the fact that the maximum energy values reached in each case is almost exactly the same, and that although the position of this maximum does not coincide, the actual magnitudes of the ΔA function (the shaded area in Fig. 6) are identical within the experimental error of determination. Thus the tensile properties of the new blacks are very similar to those of this commercial black. The blacks would legitimately be expected to behave in a similar manner in all the uses to which channel blacks are put.

Abrasion Resistance

Abrasion tests have been carried out on these samples with the du Pont Abrader (Table XI). It appears that the two blacks under test again show agreement within the experimental error.

It is of interest to note that the base mix was more difficult to abrade than the samples with low carbon black loadings. This phenomenon has

TABLE XI

ABRASION RESISTANCE

Sample	Loading	Specific gravity	Volume loss, cc. per h.p-hr.
Base mix	—	0.980	183
Pyrolysis off-gas	15	1.030	258
Standard rubber black "B"	15	1.029	245
Pyrolysis off-gas	35	1.093	232
Standard rubber black "B"	35	1.092	220
Pyrolysis off-gas	55	1.148	183
Standard rubber black "B"	55	1.142	194
Pyrolysis off-gas	75	1.190	133
Standard rubber black "B"	75	1.190	135
Pyrolysis off-gas	100	1.282	160
Standard rubber black "B"	100	1.275	163

been commented on before (13), and is out of line with the general relation existing between the concentration of a filler and the abrasion resistance. It is perhaps a spurious effect due to some lubricating power possessed by the base mix that protects it from the abrasive paper of the machine. Accelerated abrasion tests carried out by special machines of this nature are far from satisfactory, as shown by a number of investigators, and this phenomenon may be added to the list of uncertainties.

Conclusion

It has been shown that the yield of carbon black that may be obtained from any mixture of hydrocarbon gases is strongly influenced by the presence of olefines; in fact, it has appeared that in the pyrolysis of off-gas mixtures, the olefines are largely responsible for the production of carbon black. In mixtures of ethylene, methane and hydrogen, the methane may be replaced by hydrogen to a very considerable extent without an appreciable effect on the yield.

The most efficient utilization of hydrocarbon gases of the type of butane and propane for the production of carbon black by the impingement method consists of preliminary pyrolysis of the gases to produce olefines and a certain amount of polymerized aromatic liquids, with the subsequent utilization of the waste gas in a channel plant of the usual type.

It must be remembered that the yields that appear in the major part of this research do not represent the maximum values that could be obtained from the gases. If very small tips, in relation to the size of the channel, were employed, yields up to 5 lb. per 1000 cu. ft. were obtained. When the correction due to expansion is applied, a yield of 10 lb. per 1000 cu. ft. of original gas is obtained. This value represents a theoretical recovery of almost 10%, a very good value for the channel process which, of itself, can seldom achieve more than 6%. These results are made possible by the fact that the production of olefines in the pyrolysis furnace produces a partial cracking of the gas, so that in effect a smaller part of this operation must be carried out in the flame. This results in the conservation of carbon.

The carbon produced by this process is of a quality that compares favorably with the best commercial rubber blacks obtainable at present. The fact that a carbon that has proved to be so similar to a commercial black made from paraffin hydrocarbon gases may be produced in a laboratory plant by the use of a different gas, and, of necessity, an arrangement of burners very different from that used in the large-scale carbon black plants, may be regarded as a proof of the inherent simplicity of the flame impingement process. It appears that a good black may be produced if a luminous flame is made to impinge, under relatively uniform conditions productive of maximum yield. The principal factors controlling this yield are the richness of the gas, the shape of the flame, and the position of the depositing surface in the flame, the first two factors being fixed in any given case, and the last readily ascertainable.

The relation between the controllable variables of production and the subsequent properties of the carbon will form the substance of the next paper in this series.

Acknowledgment

The author wishes to acknowledge his indebtedness to Dr. A. Cambron and Mr. C. H. Bayley, who provided the gases used in this research, to Mr. G. Stewart, who carried out the rubber testing, and to Dr. G. S. Whitby, Director of the Division of Chemistry, at whose suggestion the work was undertaken.

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NOTE ON THE DIFFRACTION OF X-RAYS BY OLD SPECIMENS OF "FROZEN" RUBBER[1]

By William H. Barnes[2]

Abstract

Monochromatic X-ray pin-hole diffraction photographs of two old specimens of "frozen" rubber are described. Histories of the specimens are given. Results are compared with existing data for "frozen" rubber and for fresh stretched rubber. Detailed figures for both conditions are thus made available and confirm the reported identity of their diffraction effects.

Introduction

The object of the present note is to make available in the literature a detailed comparison of the X-ray diffraction effects from old specimens of "frozen" rubber with available data for stretched fresh rubber. Several X-ray diagrams of "frozen" rubber have been published (2, 3), and Ott (6) has recorded measurements made on a photograph of (apparently) "frozen" crepe. Although Ott's values have been confirmed in Clark's laboratory (1) they appear to be the only values readily available in the literature and are rather meagre.

Discussion

The two specimens that form the subject of the present note were examined for Dr. G. S. Whitby and were supplied by him. They will be designated A and B hereafter. A was a pale thin unsmoked sheet made in the Malay States in 1905 and kept in the Imperial Institute, London, until it was turned over to Dr. Whitby in 1925. It was then in the "frozen" condition and has, therefore, been in this condition for at least 11 yr. and probably for 30 yr. B was a piece of smoked sheet made by Dr. Whitby in 1913 and has certainly been in the "frozen" condition for 22 yr. The "thawing point" of both samples was approximately 41° C. (7, Chap. 3). This is the temperature at which, after heating for two hours, the samples lose their stiffness and become clear. The densities (15°/15°) of these "frozen" specimens were: A, 0.9436; B, 0.9347. After "thawing", by heating at 50° C. for two and one-half hours, the densities (15°/15°) dropped to—A, 0.9233; B, 0.9184. The writer is indebted to Dr. Whitby for the density determinations. As a test of this "thawing" procedure a sample of A, after being photographed in the "frozen" condition, was suspended in water at 50° C. for two and one-half hours and then rephotographed. The well defined powder pattern characteristic of diffraction diagrams obtained from "frozen" rubber was found to have been replaced by the strong single halo characteristic of unstretched fresh rubber. The spacing corresponding to this halo was about 4.7Å as compared with 4.5 Å reported by Katz (3) for "thawed" rubber and 4.6 ± 0.1 Å reported

by Mark and von Susich (5) for fresh unstretched rubber. The weak halo at 8.0 Å also observed by Mark and von Susich does not appear in the present photograph.·

Identical diagrams consisting of 13 sharply defined haloes were obtained from the two "frozen" specimens *A* and *B*. In general characteristics the photographs are typical of those usually obtained from finely powdered organic crystals.

Results

The X-ray data are summarized in Table I: first column, present note (specimens *A* and *B*); second column, Ott's values (6) for "frozen" rubber; third column, corresponding figures of Mark and von Susich (5) for stretched

TABLE I
SUMMARY OF RESULTS

A and *B*	Ott (6)	Mark and von Susich (5)	Lotmar and Meyer (4)
0.123 *s.*	0.121 *w.*	0.1251 *v.s.*	0.1225 *s.*
—	—	—	0.140 *v.w.*
0.155 *v.s.*	0.153 *s.*	0.156 *s.*	0.154 *s.*
0.183 *v.s.*	0.182 *s.*	{ 0.1851 *v.s.* 0.189 *m.*	{ 0.182 *v.s.* 0.188 *m.*
0.206 *s.*	0.192 *w.*	{ 0.194 *v.s.* 0.208 *m.* 0.212 *w.*	{ 0.205 *m.s.* 0.208 *w.*
0.226 *m.*	0.224 *w.*	{ 0.227 *m.* 0.228 *m.*	{ 0.223 *w.* 0.223 *m.*
0.255 *w.m.*	0.240 *v.w.*	{ 0.248 *m.* 0.262 *w.*	{ 0.245 *w.* 0.256 *w.*
0.277 *w.*	0.265 *v.w.*	{ — 0.279 *w.*	{ 0.270 *v.w.* 0.277 *w.*
0.298 *m.*	0.289 *v.w.*	{ — 0.293 *v.w.* 0.300 *w.* 0.308 *w.*	{ 0.299 *v.w.* 0.300 *v.w.* 0.299 *w.* —
0.319 *v.w.*	—	0.323 *v.w.*	0.322 *v.w.*
—	—	—	0.336 *v.w.*
0.345 *w.m.*	—	{ 0.350 *w.* —	{ 0.345 *v.w.* 0.350 *v.w.*
0.372 *w.m.*	—	{ — 0.375 *m.* —	{ 0.370 *w.* — 0.374 *v.w.*
0.398 *w.*	—	0.388 *w.*	0.400 *v.w.*
0.418 *v.w.*	—	—	—·-

fresh rubber; fourth column, more recent data of Lotmar and Meyer (4) for stretched fresh rubber. Data are recorded in terms of *sin θ* values for $Cu_{K\alpha}$ ($\lambda = 1.54$ Å) radiation; the figures of Ott (iron target, $\lambda = 1.93$ Å) were recalculated for copper, and those of Lotmar and Meyer ($\sin\theta/\lambda$) were multiplied by $\lambda(1.54)$. Visually estimated intensities are indicated (*m* = medium, *s* = strong, *v* = very, *w* = weak). The brackets in Columns 3 and 4 serve to group fibre spots which would lead to powder haloes unresolvable at the crystal-to-plate distances employed for the data of the first two columns. It will be seen that the agreement among the four columns is very good, and that the present more definite powder photographs of "frozen" rubber yield data in even better accord with those from stretched fresh rubber than do those of Ott (6).

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PLATE I

Debye-Scherrer rings from an old sample of "frozen" raw rubber

THE ALKALOIDS OF FUMARIACEOUS PLANTS

XIV. CORYPALLINE, CORLUMIDINE AND THEIR CONSTITUTIONS[1]

By Richard H. F. Manske[2]

Abstract

Corypalline, $C_{11}H_{15}O_2N$, a new phenolic alkaloid from *Corydalis pallida* and from the seeds of *C. aurea*, on methylation yielded the known 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline. On ethylation it yielded 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline identical with a specimen synthesized for purposes of comparison. Corypalline therefore is 2-methyl-6-methoxy-7-hydroxy-tetrahydro-isoquinoline, a synthesis of which was achieved.

Oxidative fission of corlumidine O-ethyl ether yielded a base identical with a synthetic specimen of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline. Treatment of the degradative as well as the synthetic base with alkali yielded the corresponding 1-keto-isoquinoline. Corlumidine therefore is 7-O-desmethyl-corlumine.

Syntheses of 2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline and the corresponding 1-keto-derivative are described.

During a preliminary investigation of the alkaloids of *Corydalis pallida* Pers., a Japanese species, a small amount of a phenolic alkaloid, melting at 168° C.*, was isolated, for which the name *corypalline* is now proposed. Recent work on the seeds of *C. aurea* has disclosed corypalline as one of the constituents. Analyses yielded figures in agreement with $C_{11}H_{15}O_2N$ and one methoxyl group was indicated. Methylation with diazomethane yielded a monomethyl ether, $C_{12}H_{17}O_2N$, which crystallized as the hemihydrate and which proved to be identical with 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline, previously obtained from adlumine (3) and corlumine (4). Only two structures (I, II) are therefore possible for corypalline. Ethylation
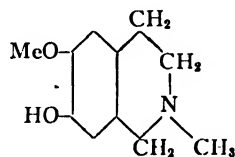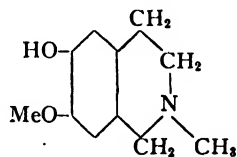
(I)   (II)

with diazoethane yielded a crystalline base, $C_{13}H_{19}O_2N$, melting at 65° C., and this proved to be identical with a synthetic specimen of 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline. The latter was prepared by methylating 6-methoxy-7-ethoxy-3 : 4-dihydro-isoquinoline (8) with methyl iodide and reducing the resultant quaternary iodide with tin and hydrochloric acid. Corypalline therefore is 2-methyl-6-methoxy-7-hydroxy-tetrahydro-isoquinoline (I).

* *Melting points are corrected.*

A synthesis of corypalline was accomplished by a route parallel to that used by Späth, Orechoff and Kuffner (10) in their synthesis of salsoline. Ring closure of the formyl derivative of β-(3-methoxy-4-benzyloxy-phenyl)-ethylamine yielded 6-methoxy-7-benzyloxy-3 : 4-dihydro-isoquinoline, which was then methylated with methyl iodide to the quaternary iodide. Reduction of the latter with tin and hydrochloric acid served, in the same operation, to remove the benzyl group. The resulting phenolic base was identical with corypalline in all respects.

With the exception of hydrohydrastinine found in minute quantity in *C. cava* (9), corypalline is the simplest alkaloid thus far found in any species of Fumariaceae, although salsoline (Chenopodiaceae) and pectenine (Cactaceae) from other sources are closely related.

In a previous communication the author proved, by methylation with diazomethane to corlumine, that corlumidine isolated from *C. scouleri* (4) possessed either one of the structures (III) or (IV). Owing to the co-presence of scoulerine (5) in the same botanical source, the expression (III) was preferred.

(III)   (IV)
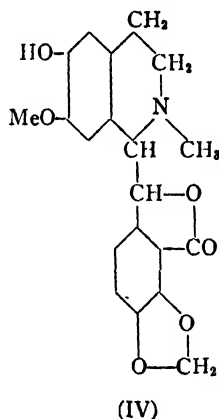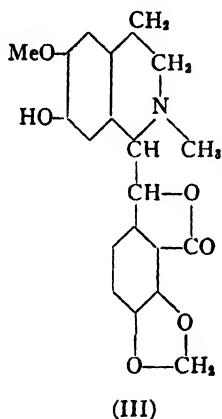
In this eventuality, corlumidine O-ethyl ether on oxidative fission may be expected to yield an amino-aldehyde which on treatment with alkali (Cannizzaro) should be convertible into corypalline O-ethyl ether, together with the corresponding 1-keto-derivative. The result of the experiment was the isolation of a base as picrate, together with the neutral product, but the picrate was not identical with that of corypalline O-ethyl ether. The obvious, though erroneous, interpretation was that corlumidine is (IV), and that the ultimate degradative base was 2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline. A synthesis of this base by a procedure strictly analogous to that of corypalline O-ethyl ether failed, however, to establish the identity of the two substances, and the synthetic 1-keto-derivative was not identical with the neutral product from corlumidine. It was ultimately realized that the result of the Cannizzaro reaction was as originally anticipated. The picrate

which was obtained, was, however, that of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline (V),

(V)   (VI)
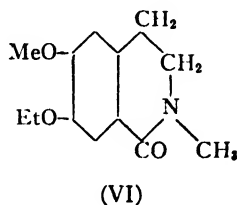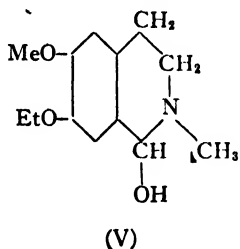
namely, the unchanged hydrolytic base. Owing to the small amounts of material available the more soluble picrate of corypalline O-ethyl ether was lost in the filtrate. A synthesis of the hydroxy-isoquinoline (V) was readily achieved by treating the methiodide obtained during the synthesis of corypalline O-ethyl ether with potassium hydroxide at low temperature. The resulting rearrangement, which is well known in bases of this type, proceeded readily, and the picrate of the synthetic base (V) was identical with that from corlumidine. Finally, the hydroxy-base (V) on treatment with alkali was converted into corypalline O-ethyl ether and the corresponding keto-compound (VI), which proved to be identical with the neutral compound obtained from corlumidine, which is, therefore, represented by (III).

The β-arylethyl-amines required in the syntheses of the methoxy-ethoxy-isoquinolines were prepared by a route involving the Curtius reaction, coupled with a conversion to the phthalimide (2) and hydrolysis of the latter with hydrazine (1).

Experimental

Methylation of Corypalline

A solution of corypalline (50 mg.) in methanol was treated with an ethereal solution of diazomethane, and after 24 hr. the organic solvents were boiled off. The residue was dissolved in dilute hydrochloric acid and the filtered solution basified with excess potassium hydroxide. The liberated base was extracted with ether, dried with potassium carbonate, and the solution evaporated to a small volume. The hemihydrate, which readily crystallized, melted at 82° C., and when admixed with a specimen from adlumine (3) the mixture melted at 82–84° C. Calcd. for $C_{12}H_{17}O_2N \cdot \frac{1}{2}H_2O$; C, 66.67; H, 8.33; N, 6.48; 2 OMe, 28.70%. Found: C, 66.56; H, 8.41; N, 6.48; OMe, 28.04%.

The picrate was recrystallized from benzene-methanol; it melted at 160° C. either alone or in admixture with an authentic specimen of 2-methyl-6 : 7-dimethoxy-tetrahydro-isoquinoline picrate.

Ethylation of Corypalline

The ethyl ether of corypalline was obtained by the procedure outlined for the preparation of the methyl ether. It crystallized with great facility, and was recrystallized from purified hexane in which it is only sparingly soluble.

Long fine needles, which melt at 65° C., were thus obtained. The picrate is sparingly soluble in cold methanol; it was recrystallized from the boiling solvent. It consisted of pale yellow fine prisms melting sharply at 136° C.

β-(3-Methoxy-4-ethoxy-phenyl)-propion-hydrazide

β-(3-Methoxy-4-ethoxy-phenyl)-propionic acid (6) was esterified with methanol in the presence of sulphuric acid and the ester was isolated in the usual way. It was purified by distillation *in vacuo*, and on cooling it solidified completely, melting sharply at 46° C. To prepare the hydrazide a mixture of 47.6 gm. of the methyl ester and 10 gm. of hydrazine was treated with sufficient methanol to yield a homogeneous solution and then heated on a steam bath in an open flask for 16 hr. The solid cake of hydrazide thus obtained was of sufficient purity for the next stage in the synthesis. A small portion was recrystallized from hot methanol in which it is moderately soluble, and the hydrazide then consisted of colorless prisms melting at 124° C. Calcd. for $C_{12}H_{18}O_3N_2$; N, 11.76%. Found: N, 11.19%.

A small amount of a very sparingly soluble by-product, melting at 201° C., was present in the hydrazide. This is evidently the diacyl hydrazide since hydrolysis with potassium hydroxide regenerated the aryl-propionic acid. The same disubstituted hydrazide was obtained as a by-product during the conversion of the hydrazide into the azide. Such a secondary course during the preparation of azides is not new and has been frequently observed by the author.

β-(3-Methoxy-4-ethoxy-phenyl)-ethylamine

The synthesis of this amine was described by Späth and Dobrowsky (8) who obtained it by way of the corresponding nitro-styrene. Intermediates were not isolated in the following synthesis. A solution of 12 gm. of the above-mentioned hydrazide in 50 cc. of acetic acid was cooled by adding crushed ice and then treated with an aqueous solution of 4 gm. of sodium nitrite. The precipitated azide soon crystallized. It was filtered off, washed with water and thoroughly drained at the pump. The somewhat pasty product was decomposed by gradual addition to boiling methanol. On cooling, a small amount of the diacyl hydrazide separated and this was filtered off. It may be noted that the azide prepared from the carefully purified hydrazide also yielded this by-product. The filtrate, which contained the methyl urethane and the dialkyl urea, was evaporated to a thick syrup. It was treated with 7.4 gm. of phthalic anhydride (2) and heated in an oil bath for 15 min. at 225–230° C. The cooled mixture was treated with a little methanol and the excess anhydride removed by adding aqueous sodium bicarbonate. The oily phthalimide was taken up in ether and the washed solution dried, filtered, and evaporated. The residue from two such experiments weighed 22 gm. It was treated with 4 gm. of hydrazine (1) in a little methanol and heated on the steam bath. Crystallization of phthalyl hydrazide was almost immediate. The methanol was boiled off and water and excess potassium hydroxide added, and the mixture exhausted with ether. The combined

extract was washed with a little water and the amine then extracted with several successive portions of dilute hydrochloric acid. Regeneration of the amine from the acid solution and extraction with ether yielded 4.0 gm.

The ethereal solution from which the amine had been extracted yielded, on drying and evaporating, an oily residue that crystallized almost completely in the course of several days. It was drained at the pump and recrystallized first from benzene-petroleum ether and then from dilute methanol; it consisted of colorless rectangular plates melting sharply at 81° C. This proved to be the N-carbomethoxy derivative of the amine, and its presence here was due to incomplete reaction with the phthalic anhydride. Calcd. for $C_{13}H_{19}O_4N$; C, 61.66; H, 7.51; N, 5.53%. Found: C, 61.76; H, 7.47; N, 5.80%.

In a second experiment the azide was extracted with ether from the acetic acid mixture. Some sparingly soluble diacyl hydrazide was removed by filtration and the ethereal solution thoroughly washed finally with aqueous sodium bicarbonate. The ether was distilled from small successive portions and the residual azide decomposed by gentle warming with water. The resulting sym-di-β-(3-methoxy-4-ethoxy-phenyl)-ethyl urea crystallized readily and when recrystallized from hot methanol it melted at 154° C. Calcd. for $C_{23}H_{32}O_5N_2$: N, 6.42%. Found: N, 6.64%.

It was converted into the phthalimide as above. Recrystallized from hot methanol, β-(3-methoxy-4-ethoxy-phenyl)-ethyl-phthalimide was obtained in colorless moderately soluble needles melting at 84° C. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31%. Found: N, 4.34%.

During the conversion of this crude phthalimide into the amine a substance sparingly soluble in ether was obtained. It was recrystallized from methanol in which it is moderately soluble; it then consisted of large colorless plates melting at 127° C. Analyses show that this is β-(3-methoxy-4-ethoxy-phenyl)-propion-β-(3-methoxy-4-ethoxy-phenyl)-ethyl amide. Calcd. for $C_{23}H_{31}O_5N$; C, 68.83; H, 7.73; N, 3.49%. Found: C, 68.48; H, 7.80; N, 3.71%.

2-Methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline

The amine described above (4.0 gm.) was converted by the procedure of Späth and Dobrowsky into 6-methoxy-7-ethoxy-3 : 4-dihydro-isoquinoline. There was obtained 2.2 gm. of crystalline base which was treated with excess methyl iodide in methanol. The solid crystalline cake of methiodide, which separated in the course of 30 hr., was dissolved in hot water, and the filtered solution heated on the steam bath overnight with 25 cc. of concentrated hydrochloric acid and finely granulated tin. The aqueous decantate was diluted somewhat and most of the tin precipitated with hydrogen sulphide. The clear filtrate from which the excess hydrogen sulphide had been removed was basified with excess potassium hydroxide and the liberated base extracted with ether. The ether extract was evaporated somewhat, filtered with the addition of a little charcoal, and evaporated to a thin syrup. The colorless crystals that separated were washed with petroleum ether and recrystallized from a mixture of ether and hexane. Washing with the latter solvent and

drying *in vacuo* yielded pure 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline melting snarply at 65.5° C., and this melting point was not depressed when the substance was mixed with a specimen of corypalline ethyl ether. Calcd. for $C_{13}H_{19}O_2N$: N, 6.34%. Found: N, 6.23%.

The picrate was recrystallized from hot methanol; it melted at 136° C. either alone or in admixture with a specimen of corypalline ethyl ether picrate.

Synthesis of Corypalline

The requisite β-(3-methoxy-4-benzyloxy-phenyl)-ethylamine was prepared from benzyl vanillin by the method described by Späth and co-workers (10). From 46 gm. of vanillin there was obtained 2.1 gm. of the amine which was treated with 2 cc. of anhydrous formic acid and heated on a steam bath for five hours. The product was heated in an oil bath at 170-180° C. for 30 min., dissolved in toluene, heated to boiling and treated with 4 gm. of phosphorus pentoxide in small successive portions. The toluene was decanted from the dark pasty residue and the latter decomposed with ice and a little hydrochloric acid. The boiled and filtered solution (charcoal) was basified with ammonia and the liberated base extracted with several successive portions of ether. Evaporation of the extract yielded the dihydro-isoquinoline which solidified on cooling. It was dissolved in a small volume of methanol and 2 gm. of methyl iodide added. After 36 hr. the solvents were evaporated and the filtered solution of the residue was treated with 15 cc. of concentrated hydrochloric acid and heated on a steam bath for 24 hr. with excess tin. The tin in the solution was removed by means of metallic zinc and the filtered solution basified with excess ammonia. The ether extract from the basic solution crystallized when evaporated to a small volume, and the base thus obtained melted at 166° C. Yield, 0.2 gm. It crystallized with great facility when a concentrated methanolic solution was treated with a little dry ether in which it is sparingly soluble. As thus obtained synthetic corypalline consisted of colorless, well formed prisms, melting sharply at 168° C. Corypalline of natural origin also melts at 168° C., and in admixture with a synthetic specimen there was no depression in melting point.

The picrate was recrystallized from hot methanol in which it is sparingly soluble. Pale yellow needles melting at 178° C. were thus obtained. A specimen of corypalline picrate prepared from the alkaloid from the seeds of *Corydalis aurea* melted at 178° C., and a mixture of the two products melted at the same temperature.

Ethylation and Degradation of Corlumidine

A suspension of 0.8 gm. of corlumidine in 50 cc. of chloroform was treated with an ethereal solution of diazoethane. Evolution of nitrogen and dissolution of the alkaloid gradually ensued. After 24 hr. the ether was boiled off and a second portion of ethereal diazoethane added. When the alkaloid was completely dissolved and the evolution of nitrogen ceased, the solution was evaporated to dryness and the residue dissolved in dilute hydrochloric acid. The filtered solution was basified with ammonia and the liberated base ex-

tracted with a mixture of ether and chloroform. Removal of the solvent yielded an almost colorless resin which failed to crystallize in contact with methanol. The solvent was completely removed *in vacuo* and the corlumidine ethyl ether heated for 20 min. with 8 cc. of dilute nitric acid prepared by diluting 2 cc. of concentrated nitric acid to 10 cc. with water. The cooled solution was rendered alkaline by the addition of excess potassium hydroxide and the basic hydrolytic fragment extracted with ether. Parenthetically it may be mentioned that the alkaline solution on appropriate treatment readily yielded 3 : 4-methylene-dioxy-phthalide, a rather superfluous observation, but nevertheless a confirmation of the structure of the phthalide moiety. The ether extract was freed of solvent and the basic residue heated with methanolic potassium hydroxide on the steam bath for one hour. Water was added and the methanol boiled off. The insoluble oil was taken up in ether and the solution cautiously washed with water. It was then shaken with several successive portions of dilute hydrochloric acid and the base regenerated from the acid extract. It was again taken up in ether and the residue from this dissolved in boiling hexane. The filtered extract was evaporated to a small volume but did not crystallize readily. It was converted into the picrate which was recrystallized from hot methanol in which it is sparingly soluble. Orange-yellow fine prisms of 1-hydroxy-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline picrate, melting at 180° C., were thus obtained.

The ether solution from which the above base had been extracted was dried with potassium carbonate and the ether largely distilled. Cautious addition of hexane yielded large colorless plates of 1-keto-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline melting sharply at 121° C.

1-Hydroxy- and 1-Keto-2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline

The methiodide from 2.0 gm. of 6-methoxy-7-ethoxy-dihydro-isoquinoline was dissolved in a small volume of water, and the cooled solution rendered strongly alkaline by the gradual addition of potassium hydroxide. The semi-solid precipitate was separated from the alkaline solution by repeated extraction with ether. Removal of the ether yielded a pale yellow, partly crystalline mass.

A small portion of this was converted into the picrate in hot methanol, and the orange crystals which were thus obtained melted at 181° C. In admixture with the picrate from the degradation of corlumidine, there was no depression in the melting point. Calcd. for $C_{19}H_{22}O_{10}N_4$: N, 12.02%. Found: N, 12.40%.

The remainder of the base was heated for several hours on the steam bath with aqueous methanolic potassium hydroxide and then the methanol evaporated. The residue was extracted with several successive portions of ether and the combined extract washed with water. It was then extracted with dilute hydrochloric acid, from which extract a small amount of 2-methyl-6-methoxy-7-ethoxy-tetrahydro-isoquinoline was isolated, but only with difficulty. The ethereal solution was evaporated and the crystalline residue recrystallized from dry ether. Colorless elongated plates of 1-keto-2-methyl-

6-methoxy-7-ethoxy-tetrahydro-isoquinoline were thus obtained. This substance, either alone or in admixture with a specimen of the neutral degradative product from corlumidine, melted sharply at 121° C., and the melt readily crystallized again on slight cooling. Calcd. for $C_{13}H_{17}O_3N$; N, 5.96%. Found: N, 6.14%.

Isovanillin Ethyl Ether

The ethylation of isovanillin with diethyl sulphate does not appear to have been previously described. A suspension of 30.4 gm. of isovanillin in 34 gm. of diethyl sulphate is treated with 10 cc. of ethanol and a concentrated aqueous solution of 12 gm. potassium hydroxide slowly added with vigorous agitation. Toward the end of the addition gentle heating is desirable and a little more potassium hydroxide may be added to ensure alkalinity of the mixture. The oil is extracted with ether, washed with aqueous potassium hydroxide and with water. Removal of the ether and drying on a steam bath yields an almost colorless residue which solidifies completely on cooling and weighs 35 gm. (97% of theory). On distillation *in vacuo* it may be obtained colorless and the yield then is 31–32 gm. Oxidation with alkaline permanganate yielded the known 3-ethoxy-4-methoxy-benzoic acid melting at 165° C.

β-(3-Ethoxy-4-methoxy-phenyl)-propionhydrazide

The methyl ester of the propionic acid (6) was readily prepared in 90% yield by esterification in the presence of sulphuric acid. It was obtained as a colorless viscous liquid boiling at 166° C. at 4 mm. The methyl ester (43 gm.) was heated on a steam bath for 16 hr. with hydrazine (11 gm.) and a little methanol. The completely solid residue was of sufficient purity for the preparation of the azide. A portion was recrystallized from hot methanol in which it is readily soluble. Colorless fine needles, melting at 124° C., were thus obtained. Calcd. for $C_{12}H_{18}O_3N_2$: N, 11.76%. Found: N, 11.19%.

β-(3-Ethoxy-4-methoxy-phenyl)-ethylamine

The azide was prepared by the procedure outlined in the case of the isomer, but owing to the fact that it did not crystallize it was extracted with ether. At this point a small amount of the diacyl hydrazide separated in the aqueous phase. The ethereal solution was washed with water and then with aqueous sodium bicarbonate. A small portion of the ether extract was evaporated and the residue decomposed by gentle heating with water. The accumulated dialkyl-urea served as a diluent for the decomposition of subsequent portions of the azide which were added progressively until a total of 42 gm. of hydrazide had been used. The oily product was finally dissolved in ether and filtered from a further small amount of diacyl-hydrazide. Evaporation of the solvent from the filtrate yielded a residue weighing 20 gm. This product, which consisted essentially of the dialkyl-urea, was worked up as in the case of the isomer. It yielded 5.2 gm. of the arylethylamine.

Sym-Di-β-(3-ethoxy-4-methoxy-phenyl)-ethyl Urea and the Phthalimide

The crude urea in contact with ether readily crystallized. It was washed with ether and recrystallized from hot methanol in which it is readily soluble. Large colorless prisms, melting at 137° C., were thus obtained. Calcd. for $C_{23}H_{32}O_5N_2$: N, 6.42%. Found: N, 6.94%.

When the urea is heated with phthalic anhydride under the standard conditions, it is converted into the corresponding phthalimide. The latter was isolated in the usual way and when recrystallized twice from hot methanol, long, stout needles were obtained. β-(3-Ethoxy-4-methoxy-phenyl)-ethyl phthalimide is sparingly soluble in cold methanol and melts at 116° C. Calcd. for $C_{19}H_{19}O_4N$: N, 4.31%. Found: N, 4.35%.

2-Methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline

The procedure detailed in the case of the 6-methoxy-7-ethoxy analogue yielded 2.2 gm. of 6-ethoxy-7-methoxy-3 : 4-dihydro-isoquinoline from 5 gm. of the above-mentioned amine. It was converted into the methiodide with methyl iodide. A portion of the latter was reduced with tin and hydrochloric acid. The resulting tertiary base crystallized readily, and when recrystallized from dry ether it consisted of long needles and melted sharply at 76° C. Calcd. for $C_{13}H_{19}O_2N$: C, 70.59; H, 8.60; N, 6.34%. Found: C, 70.51; H, 8.54; N, 6.26%.

The picrate is moderately soluble in methanol. It crystallized from this solvent in pale yellow plates melting at 120° C.

1-Keto-2-methyl-6-ethoxy-7-methoxy-tetrahydro-isoquinoline

A second portion of the methiodide, from which the above tertiary base was prepared, was treated with solid potassium hydroxide in concentrated aqueous solution. The liberated base was extracted with ether and then heated with aqueous methanolic potassium hydroxide to bring about the Cannizzaro change. The basic portion of the reaction product was isolated as the picrate, which proved to be identical with that obtained by reducing the quaternary iodide. The neutral fraction crystallized readily and when recrystallized from ether it was obtained in colorless thick plates melting at 96° C. Calcd. for $C_{13}H_{17}O_3N$: N, 5.96%. Found: N, 5.94%.

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A FURTHER STUDY OF THE PRETREATMENT OF WOOD IN AQUEOUS SOLUTIONS[1]

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Abstract

The study of the pretreatment of wood has been continued. Wood-meal was heated in buffer solutions at constant temperature for periods of time up to 96 hr. This extreme pretreatment was found to cause the formation of a substance which is determined as lignin by the ordinary methods of analysis. It was found that wood, heated in a buffer solution at pH 3 for 36 hr. at 140° C., could be completely delignified, though at a reduced rate of pulping. Jack pine is shown to give results similar to those obtained with spruce. A physical agglomeration of the lignin particles is proposed as an explanation of the results.

In two previous papers (2, 3) the influence of the heating of wood in aqueous solutions on the rate of its subsequent delignification in sulphite liquor was discussed. On the basis of the experimental data cited, the hypothesis was advanced that the heating of wood in aqueous solutions results in a physical agglomeration of the lignin present, and hence in a reduction of the surface area available for reaction. In the sulphite process this tendency would constantly oppose an acceleration in the cooking rate, which would normally be expected as the sizes of the individual lignin particles were decreased through reaction. The action of these two opposing tendencies was advanced as a possible explanation for the approximately monomolecular rates observed in delignification with sulphite solutions.

If the pH at which the minimum pretreating effect was observed differed from that of sulphite liquor at the cooking temperature, and if the temperature coefficients of the dissolving process and the coagulation-process are different, it might be possible to detect a slowing up of the cooking reaction, brought about by a coagulation of the lignin during cooking in sulphite liquor.

The following experiment was designed to test this. Delignification curves for 120° and 140° C. were obtained with chips from the same wood specimen. With a sample of the same wood, a cook was carried out for six hours at 120° C. under conditions identical with those obtaining during the series at 120° and 140° C. After six hours the oil bath was quickly lowered, and a second bath, heated to 140° C., was raised about the cooking cell. The cooking was then continued at the latter temperature for two hours.

In order to make this experiment more easily intelligible a diagram to illustrate the curves at 120° and 140° C. is shown in Fig. 1.

The wood sample was cooked at 120° C. for six hours. It should then have a lignin value given by the point A on the curve for 120° C., which corresponds

to B on the curve for 140° C.   From the position of B, the time required to cook to this lignin value at 140° C. could be determined from the delignification curve for 140° C.   After two hours' cooking of the product A at 140° C., the equivalent time of cooking at 140° C. for the whole experiment will be
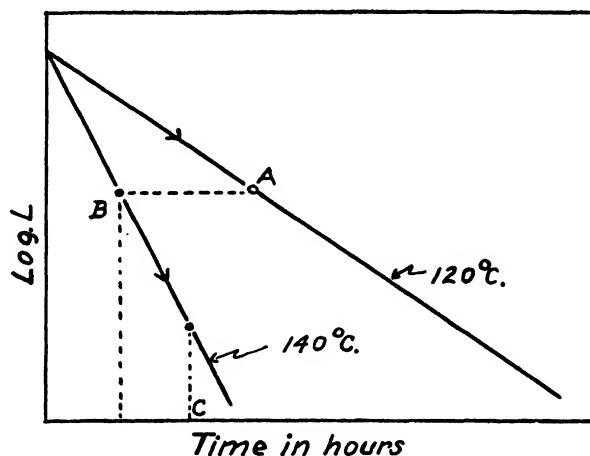
Time in hours
FIG. 1.

given by the position of C.   Now if the slow cooking period at 120° C. has favored coagulation of the lignin, the rate of cooking at 140° C. will be less than normal, and the lignin value found for the pulp will be greater than would be obtained if the cooking were actually carried out for C hours at 140° C.   The lignin value corresponding to C hours of digestion at 140° C. was found from the curve to be 1.55%.

The lignin value found in this experiment was 1.5%, which was virtually identical with the value that would be obtained if all the cooking had been done at 140° C. for an equivalent length of time.   This result agrees with the work of Yorston (10) on the effect of gradual heating in sulphite pulping.   He shows that only a very slight, if any, "pretreatment effect" can be detected in this manner.

It would appear that if there is a tendency for the lignin to coagulate during sulphite pulping, the temperature coefficient of this process must be approximately the same as that of the opposing cooking action.

The Variation of Pretreatment Effect with Temperature at Constant pH

The preceding discussion indicates the desirability of gaining further information concerning this change in lignin, which for convenience may be called the pretreatment effect.   By pretreating wood-meal in buffer solutions the hydrogen ion concentration could be kept constant and the effect of the temperature alone could be observed.

Samples of spruce wood-meal were pretreated in buffer solutions of pH 3, 5, and 7 for six hours at temperatures of 100°, 110°, 120°, 130°, and 140° C. The pretreatment was carried out in glass-lined bronze bombs.*   After the

pretreatment the samples were cooked for three hours at 140° C. in bisulphite liquor of composition: total SO_2, 5.12; free SO_2, 3.90; combined SO_2, 1.22%. The wood-meal had a density of 0.39 and a lignin content of 30.9%. The results obtained are listed in Table I.

TABLE I

VARIATION OF PRETREATMENT EFFECT WITH TEMPERATURE AT CONSTANT pH

pH of pretreating solution	Temp. of pretreatment, ° C.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %
	100	49.8	47.0	5.64	2.81
	100	49.7	46.8	5.86	2.91
3	110	50.0	46.7	6.69	3.34
	110	50.8	47.4	6.64	3.38
	120	53.2	47.4	11.00	5.84
	130	57.0	47.5	16.55	9.46
	100	49.2	46.9	4.77	2.35
	110	49.8	47.5	4.60	2.29
5	120	52.4	48.5	7.47	3.91
	130	55.1	49.3	10.35	5.81
	140	58.9	50.3	14.60	8.60
	100	53.0	49.9	5.83	3.09
	110	54.1	50.0	7.58	4 10
7	130	60.0	52.6	12.4	7.40
	140	64.6	52.6	18.6	12.0

The solutions obtained in the pretreatments at pH 3 were checked with a quinhydrone electrode after the pretreatment, and were found to have a pH of about 3.1.

The yields of pulp and the residual lignin values are plotted against the temperature of pretreatment in Fig. 2. As would be expected, the yields at pH 7 are higher than those at pH 3 or pH 5, the cellulose being less stable in acid media. It is strange, however, that the yields of carbohydrate at pH 5 and pH 7 should increase with increase in the temperature of pretreatment. It is possible that this phenomenon may be due to a shift of the pH toward the alkaline side as the temperature is increased. Another peculiar circumstance found in this series is the fact that the lignin curves for pH 3 and pH 7 cross at low temperatures. Check runs were made at 100° and 110° C. in solutions of pH 3, since these results might have been in error owing to a small temperature variation; however, the original results were found to be correct.

The lignin values obtained from the samples that were pretreated in solutions of pH 5 at 100° and 110° C. are of the same order as those that would be obtained with no pretreatment, but at higher temperature the lignin values increase, even for the pretreatments at pH 5. There apparently is no hydrogen ion concentration at which wood may be heated in a buffer solution to temperatures above 120° C. without changing the cooking properties of the
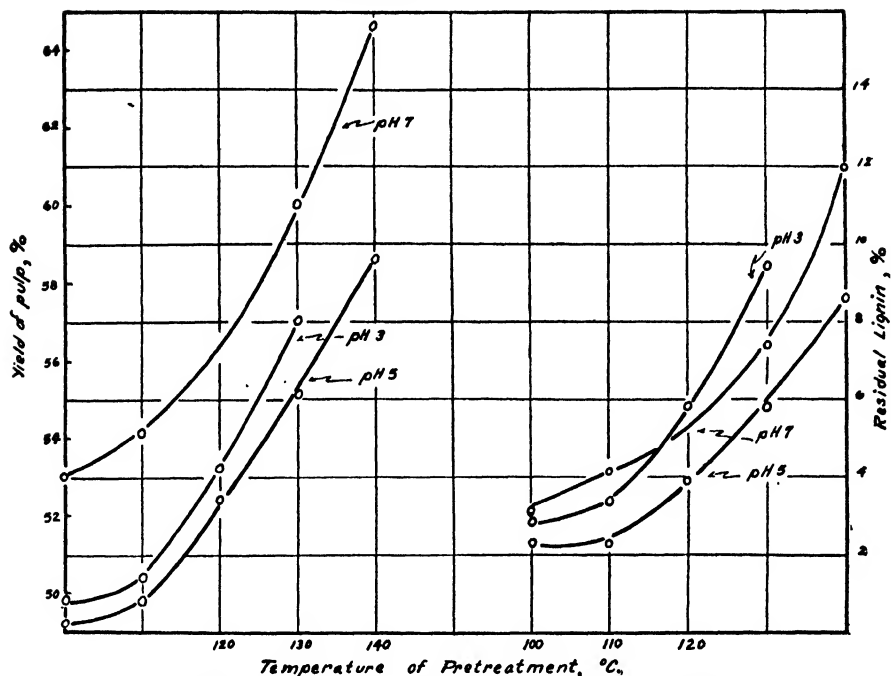
FIG. 2.   *Effect of temperature of pretreatment on subsequent delignification.*

wood to some extent, but, with the McIlvaine buffers used in these experiments, the least effect is always obtained at pH 5, as determined at room temperature.   This condition might not always hold if different buffers were used, for two reasons:

(i) Different buffer solutions of the same initial pH value may be altered to different degrees by the high temperature of pretreatment.

(ii) The effect may be due to the concentrations of the different ions present, in which case different ionic species will affect the process to different degrees.   An investigation of this factor has been published separately (1).

From the slopes of the curves in Fig. 2 it appears that the temperature coefficient of the pretreatment effect is roughly of the same order as the temperature coefficient of delignification, and the two effects are not separated in this experiment, so that no quantitative determination can be made. The similarity in value of these two temperature coefficients would make it very difficult to detect the presence of a tendency for the lignin to coagulate in normal sulphite cooking.

The Variation in Lignin Value with Time of Pretreatment at Constant Temperature and pH

Thus far the experiments on the pretreating of wood had been confined to six-hour periods, and it was of considerable interest to determine to what extent the rate of subsequent delignification would be retarded if the pre-

treating process were carried out for longer periods of time. If the pretreatment is carried out sufficiently long a maximum effect is approached, after which further pretreatment will not measurably increase the difficulty of delignifying the wood in sulphite liquor. The determination of the time required to reach this maximum, and the extent to which the lignin will be altered when the maximum is reached, might shed some light on the mechanism involved, and indicate whether it is a chemical or a colloidal change that is taking place.

To this end a series of pretreatments was carried out on samples of spruce wood-meal in solutions of pH 3 and pH 7 at 130° C. After the required period of pretreatment the samples were air-dried, and cooked for three hours at 140° C. in cooking liquor of composition as follows: total SO_2, 5.15; free SO_2, 3.90; combined SO_2 1.25%.

The results of these experiments are reported in Table II.

TABLE II

SPRUCE WOOD-MEAL PRETREATED FOR LONG PERIODS OF TIME IN BUFFER SOLUTIONS AT 130° C.

Time of pretreatment, hr.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
A. Pretreatment solutions of pH 3. Wood: density, 0.39; lignin content, 30.9%						
2	47.2	44.7	5.3	2.5		
4	53.8	46.9	12.7	6.9		
8	58.7	48.6	17.2	10.1		
12	64.3	48.4	24.7	15.9	1.26	5.10
18	65.9	47.8	27.4	18.1	1.34	4.92
24	66.7	46.9	29.7	19.8	1.36	4.57
48	67.3	43.4	35.5	23.9	1.08	3.05
B. Pretreatment solutions of pH 7. Wood: density 0.34; lignin content, 29.0%						
					pH before	pH after
2	56.2	52.0	7.5	4.21	7.01	6.94
5	60 9	53.6	11 9	7 25	7 01	6.87
8	62.5	53.6	14.3	8.94	7.01	6.87
12	66.0	54.8	17.0	11.2	7.01	6.87
18	66.2	51.8	21.7	14.3	7.01	6.83
24	68.4	52.7	23.0	15.7	7.01	6.80

The lignin values in Table II, *A*, indicate that the pretreating process has not reached a maximum, even after 48 hr. of pretreatment. The amount of lignin remaining in the pulp after three hours of digestion in sulphite liquor increases as the time of pretreatment is increased, and shows no evidence of reaching a point where further pretreatment will not increase the difficulty of delignifying the wood. This fact is emphasized in Fig. 3. Some further information is gained from the sulphur determinations. These values show that the degree of sulphonation of the lignin is decreased by continued pretreatment, and the longer the process is continued, the less sulphonation will be obtained after three hours' cooking in sulphite liquor.
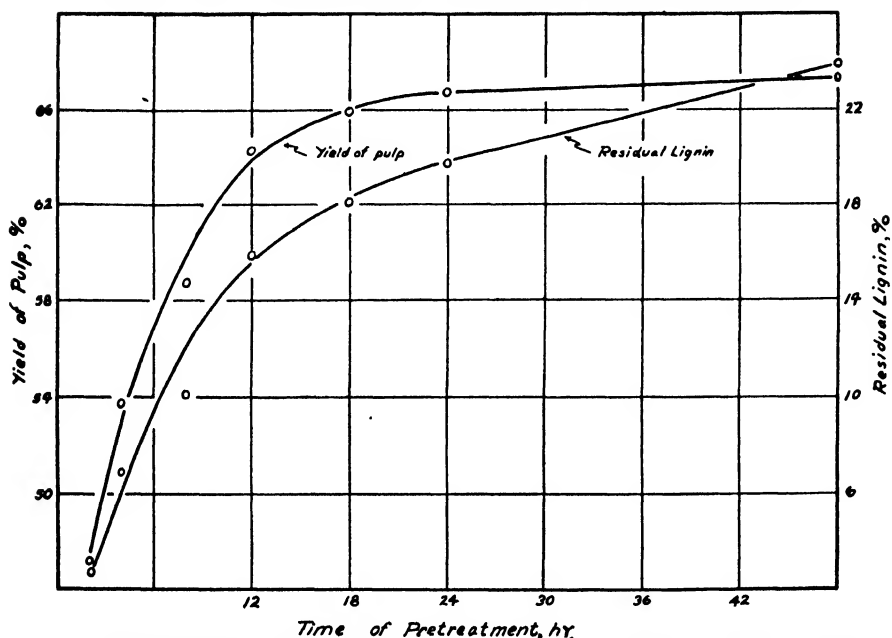
FIG. 3.   *Effect of time of pretreatment (pH 3; temp. 130° C.) on subsequent delignification.*

This series could not be continued because no more wood-meal of this sample remained.

The results listed in Table II, *B*, are plotted in Fig. 4.   It should be remarked here that this series is a repetition of work previously reported.
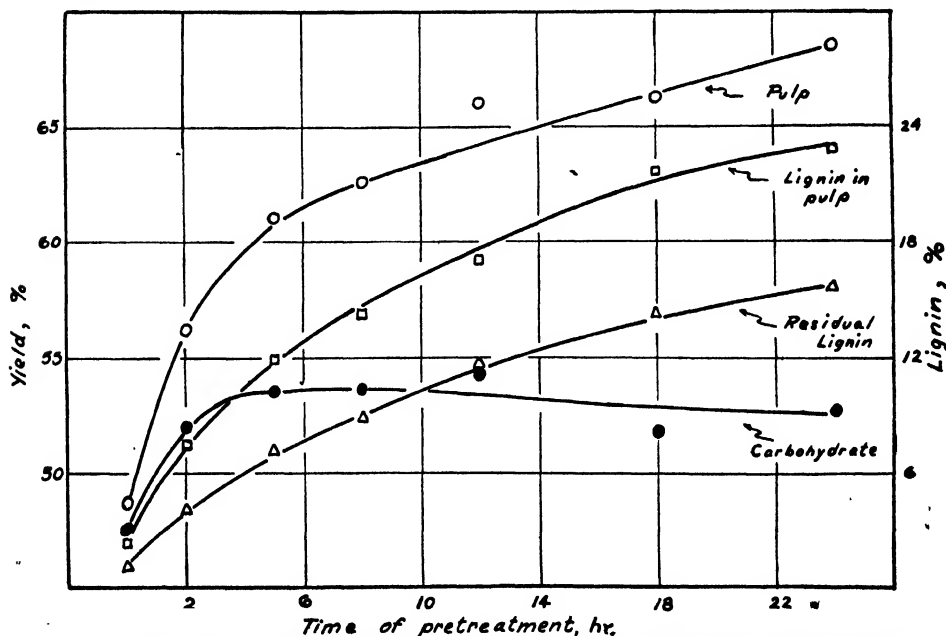
FIG. 4.   *Effect of time of pretreatment (pH 7; temp., 130°C.) on subsequent delignification.*

The experiment carried out previously (3) at pH 7 for eight hours appeared to indicate that the pretreating effect accelerated with increase in time of pretreatment. Such a phenomenon was in disagreement with the results at pH 3 and quite unexplainable. The present experiment at pH 7 carried out for 24 hr. shows a de-acceleration of the pretreating effect with increase in time of pretreatment, in complete agreement with the results at pH 3, the difference in severity being due only to the difference in pH.

It is noted that the yield of carbohydrate first increases with the time of pretreatment, reaches a maximum, and then slowly decreases. The decrease in the yield of carbohydrate after many hours of pretreatment may be due to degradation during pretreatment, simultaneous with the change that decreases the solubility of the lignin. On the other hand, it is possible that the concentration of lignin sulphonic acid in the pulp governs the yield of carbohydrate. After pretreatment the lignin sulphonates more slowly, and hence the carbohydrate material is subjected to a lower acidity within the fibres, and is less degraded in the early stages of pretreatment.

Pretreatment at 140° C.

Since the above experiments indicated that it might be necessary to continue the pretreatments for many hours before a maximum was attained at 130° C., a new supply of spruce wood-meal was prepared, and a series of pretreatments was carried out at 140° C. in solutions buffered to pH 3. The samples were then washed, air-dried, and cooked three hours at 140° C. in cooking liquor of composition: total SO_2, 5.14; free SO_2, 3.90; combined SO_2, 1.20%. A test cook was made on the untreated wood-meal.

The results listed in Table III provide a considerable amount of interesting information. The yields of pulp are seen to increase rapidly up to 18 hr. of pretreatment, and to continue increasing slowly up to a maximum at 72 hr. of pretreatment. After 96 hr. of pretreatment virtually the same yield is obtained after three hours' digestion in sulphite liquor as was obtained after 72 hr. of pretreatment. However, it is obvious that further pretreatment will cause the yields to decrease, since the yields of carbohydrate are being decreased by the severity of the pretreating process.

TABLE III

SPRUCE WOOD-MEAL PRETREATED IN BUFFER SOLUTION, pH 3, 140° C.

Time of pretreatment, hr.	Yield of pulp, %	Yield of carbohydrate, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %	Madison lignin in pulp, %	Madison residual lignin, %	Sulphur, % of pulp	Sulphur, % of Ross-Potter lignin
0	48.3	47.0	2.58	1.25			0.331	13.4
6	61.9	50.0	19.2	11.9			1.18	6.15
18	66.8	45.1	32.5	21.7	31.8	21.3	1.21	3.73
24	66.8	43.9	34.2	22.9			1.20	3.50
48	67.8	39.6	41.5	28.2	35.3	23.9	1.08	2.61
62	69.0	39.0	43.6	30.0			0.945	2.17
72	70.4	37.8	46.2	32.6			1.10	2.39
96	70.2	36.2	48.4	34.0	39.9	28.1	0.80	1.65

Wood-meal, density, 0.34; lignin content, Madison method, 26.3%; Ross-Potter method, 29.0%.

The lignin values obtained in this series were remarkable. As has been stated previously, by "residual lignin" is meant the quantity of lignin remaining in the pulp after cooking, expressed as a percentage by weight of the original wood sample; or simply—

% Residual lignin = % lignin in pulp × % yield of pulp.

Thus the limiting value for the residual lignin will correspond to the lignin content of the uncooked wood. Table III shows that, after 62 hr. of pretreatment, followed by three hours' cooking at 140° C., not only has no lignin been removed from the wood, but the residual lignin has increased to a value 1% greater than the original lignin content of the wood. On pretreating for longer periods the residual lignin values continue to increase until, after 96 hr. of pretreatment, the residual lignin reaches a value of 34%. One would gather from these results that there is being formed from the wood, either during the pretreatment or the subsequent cooking, some substance that is determined as lignin by the method of Ross and Potter (8). As a check on the above method, lignin analyses were carried out on the 18, 48, and 96 hr. samples, by the use of the Madison method. The results of these analyses (Table III) show that the sample pretreated for 96 hr. had a residual lignin value 2% greater than that of the uncooked wood, as determined by this method; namely, 26.3%. Evidently a small quantity of this "apparent lignin" is determined even by the Madison method.

The results of the sulphur determinations for this series confirm the previous statement that pretreatment of wood in aqueous solutions at high temperatures makes the lignin more difficult to sulphonate.

The yields of pulp, carbohydrate, residual lignin, and sulphur values are plotted against the time of pretreatment in Figs. 5 and 6. The curves of the
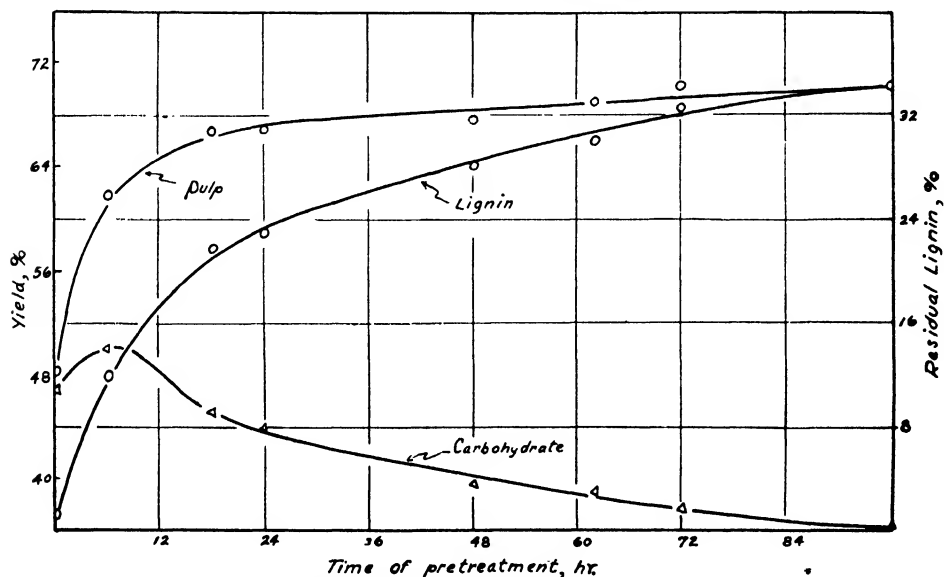
FIG. 5.   *Effect of time of pretreatment (pH 3; temp. 140° C.) on subsequent delignification.*
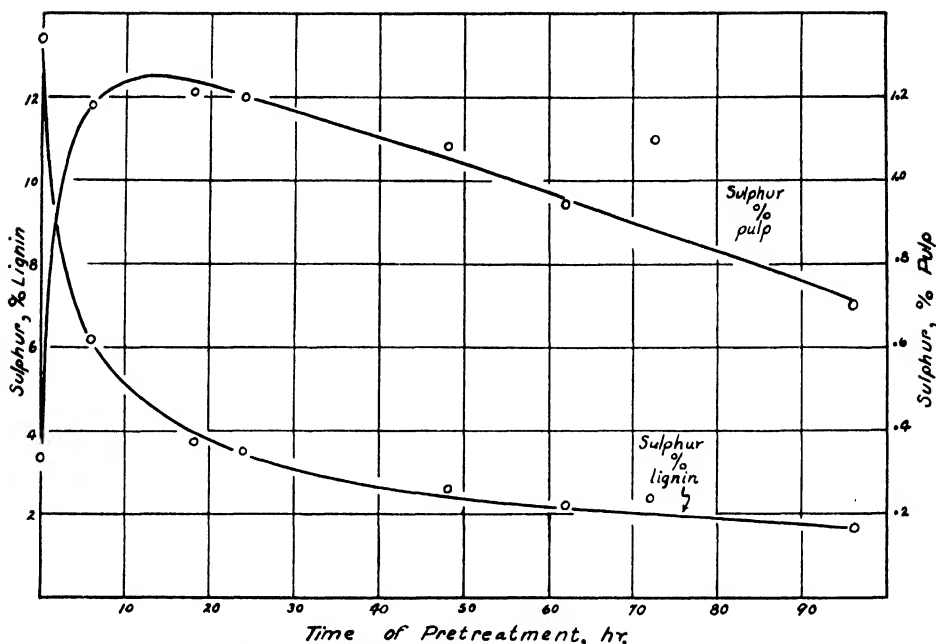
FIG. 6.   *Effect of time of pretreatment (pH 3; temp. 140° C.) on subsequent sulphonation.*

sulphur values are particularly interesting.   The first few hours of pretreat-
ment cause a marked decrease in the amount of sulphonation that can be
obtained by three hours of cooking.   Further pretreatment causes the curve
to drop more slowly.   The curve of the amount of sulphur expressed as
percentage of the pulp is similar in shape to the curve obtained in a normal
cooking series, except that the drop after the maximum is reached is more
gradual, owing to the fact that very little lignin is being cooked out after
24 hr. of pretreatment.

Investigation of the Formation of Apparent Lignin

In order to obtain a correction for the lignin values in Table III the following
experiment was performed.   Samples of the same wood-meal as that used in the
previous experiment were pretreated in solutions of pH 3 at 140° C. for 12,
24, 48, 72, and 96 hr.   The yields and lignin content of the product were
determined, after the pretreatment, as percentage of the uncooked wood-meal.

Lignin determinations by the Madison method were also carried out on
the samples that were pretreated 12, 48 and 96 hr.   The complete results
are listed in Table IV.

An experiment was also made to determine how the formation of apparent
lignin varied with the hydrogen ion concentration of the pretreating solution.
Samples of wood-meal were heated in solutions of pH 2.2, 5.0 and 8.0 for
48 hr., but, since the temperature rose to 148° C. during the pretreatment,
these results are not comparable with the results of the 48 hr. pretreatment
at pH 3, described above.

TABLE IV

THE FORMATION OF APPARENT LIGNIN DURING HEAT PRETREATMENT IN AQUEOUS SOLUTIONS

Time of pretreatment, hr.	Yield of pulp, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %	Madison lignin in pulp, %	Madison residual lignin, %
0	100	29.0	29.0	26.3	26.3
12	74.4	40.5	30.1	35.9	26.7
24	72.5	42.4	30.8		
48	71.5	44.3	31.7	38.2	27.3
72	71.3	46.3	33.0		
96	71.3	47.7	34.0	40.1	28.6

The lignin was determined by the method of Ross and Potter. The results are shown in Table V.

TABLE V

EFFECT OF pH ON THE FORMATION OF APPARENT LIGNIN

Time of pretreatment, hr.	pH of solution	Yield of pulp, %	Ross-Potter lignin in pulp, %	Ross-Potter residual lignin, %
48	2.2	66.8	50.0	34.4
48	5.0	85.2	37.6	32.0
48	8.0	82.6	36.5	30.1

If the residual lignin values reported in Table IV are plotted against the time of pretreatment, two straight lines are obtained, one for the Madison values, the other for the values obtained by the method of Ross and Potter. This is shown in Fig. 7. Although the formation of apparent lignin, as deter-
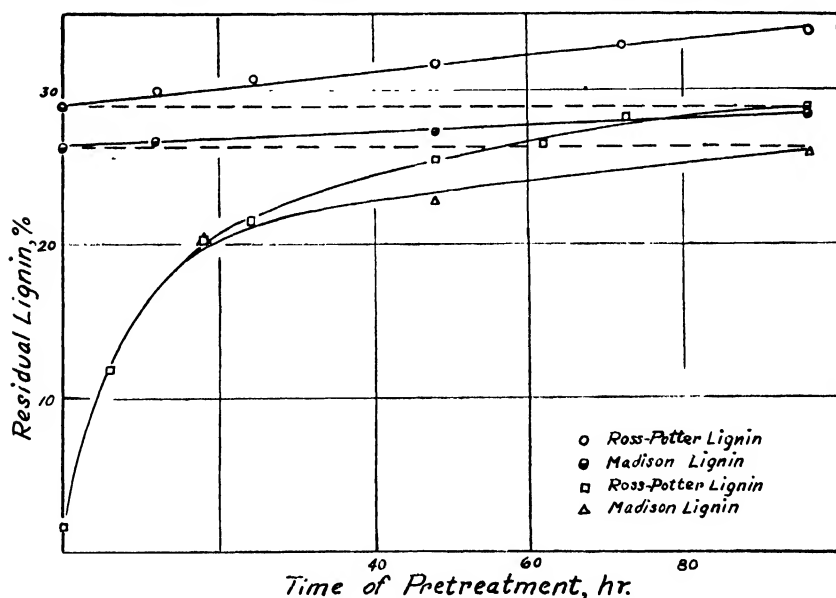
FIG. 7. *Effect of time of pretreatment (pH 3; temp. 140° C.) on the formation of apparent lignin.*

mined by both methods, increases linearly with time of pretreatment over the range investigated, the amount determined by the Madison method is much less than that determined by the method of Ross and Potter.

After 96 hr. of pretreatment the same lignin value was obtained on the uncooked sample as that obtained (see Table III) after three hours of cooking in bisulphite liquor, and this statement holds, irrespective of which method was used to determine the lignin. It appears, therefore, that pretreatment for 96 hr., under these conditions, makes subsequent delignification so slow that no loss of lignin is apparent after three hours of cooking at 140° C. Further, the apparent lignin produced in the pretreatment is evidently not cooked out in bisulphite solutions, hence there is some justification for applying a direct correction, obtained from the apparent lignin correction curve (Fig. 7), to the residual lignin values in Table III. Curves of these corrected lignin values are also plotted in Fig. 7. The corrections do not become very appreciable until after 24 hr. of pretreatment, so that former pretreatment series require no correction. However, the values in Table III are considerably altered when allowance is made for the apparent lignin formed in the pretreatment. The results were recalculated on the corrected basis, and are listed in Table VI.

TABLE VI

CORRECTED VALUES FROM TABLE III

Time of pretreatment, hr.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
0	48.3	47.0	2.58	1.25	0.33	13.4
6	61.9	50.2	18.8	11.7	1.18	6.28
18	66.8	46.1	30.9	20.7	1.21	3.91
24	66.8	45.2	32.3	21.6	1.20	3.71
48	67.8	42.2	37.8	25.6	1.08	2.86
62	69.0	42.3	38.7	26.7	0.94	2.44
72	70.4	41.8	40.6	28.6	1.10	2.71
96	70.2	41.2	41.3	29.0	0.80	1.93

The variation in the quantity of apparent lignin formed during pretreatment in solutions of different hydrogen ion concentration was almost linear, as is shown in Table V. The greatest effect was obtained with the more acid solutions.

No attempt was made in this work to identify the substance from which the apparent lignin was formed. The formation of such lignin-like substances has, however, been noted before. Norman and Jenkins (7) found that pentose, when treated with cold 72% sulphuric acid and boiled in dilute sulphuric acid, yielded a quantity of material that was determined as lignin by the accepted methods. Hawley and Harris (5) heated Cross and Bevan cellulose, prepared from spruce wood, in glass tubes for several days at 135° C. Large

quantities of lignin-like material were formed, apparently from the hexosans in the wood.   The product was designated synthetic lignin because many of the characteristics of true lignin were displayed by it.

The Rate of Delignification of Wood-meal Pretreated 36 hr. at 140° C.

It was desirable to prove conclusively that wood, pretreated in an aqueous medium for long periods, could be delignified if the cooking were continued for a sufficient length of time.

A large quantity of wood-meal, ·the same as that used in the previous experiments, was heated in a two-litre, Allegheny metal digester for 36 hr. at 140° C. in a solution of pH 3.   Five-gram samples of this pretreated wood-meal were cooked for 3, 6, 9, and 12 hr. at 140° C. in liquor of composition: total SO_2, 5.00; free SO_2, 3.88; combined SO_2, 1.12%.   Longer periods of cooking were attempted, but the liquor decomposed after 12 hr., and sulphur was precipitated into the pulp.   Longer digestion was finally attained by cooking the wood-meal nine hours, removing the bombs, and replacing the waste liquor with fresh liquor.   The digestion could be continued for 21 hr. by this two stage process.

The results shown in Table VII indicate that the change in the lignin brought about by the pretreatment hinders, but does not prevent, subsequent cooking.   It is evident that more than 2.63% of the lignin originally present

TABLE VII

WOOD-MEAL PRETREATED IN A SOLUTION OF pH3 FOR 36 HR. AT 140° C.

Length of cook, hr.	Yield of pulp, %	Carbo-hydrate, %	Lignin in pulp, %	Residual lignin, %	Sulphur as	
					Per cent pulp	Per cent lignin
3 .	69.0	46.5	32.6	22.5	1.21	3.72
6	62.6	45.0	28.1	17.6	1.35	4.81
9	54.6	42.7	21.8	11.9	1.56	7.14
12	46.3	42.0	9.3	4.32	1.40	15.0
9 + 3	49.9	42.8	14.2	7.08	0.76	5.35
9 + 6	47.4	42.3	10.7	5.06	0.57	5.31
9 + 9	44.3	41.4	7.85	3.52	0.41	5.18
9 + 12	44.0	41.6	5.98	2.63	0.31	5.26

NOTE:—*Lignin content of wood: (a) before pretreatment, 29.0%; (b) after pretreatment, 33.9%.*

in the wood must have been affected during the pretreating, yet the lignin is reduced to this value after 21 hr. of cooking, and the lignin curve (Fig. 8) indicates that longer cooking would remove more lignin.

Several interesting features are shown in this series.   It is noted that the logarithm of the residual lignin values, in the second stage of the cooking, gives a straight line.   A discontinuity is evident in the sulphur values, the
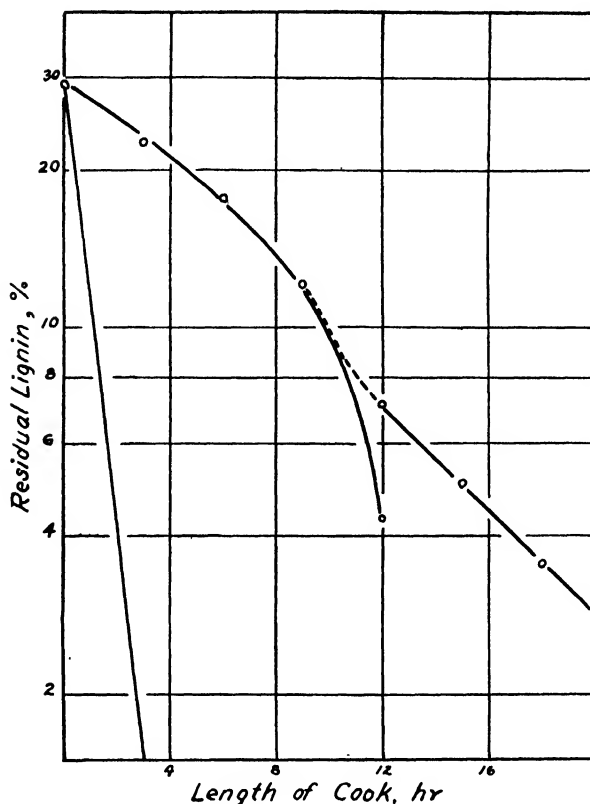
FIG. 8. *Rate of delignification of untreated wood-meal and wood-meal pretreated for 36 hr. at pH 3 and 140° C.*

sulphur as a percentage of the lignin becoming constant in the second stage. Evidently no further sulphonation occurred after the fresh liquor was introduced, and no explanation can be advanced to explain this phenomenon. Further investigation of this discontinuity in the sulphur values would be very interesting, but no time was available to continue the experiments. The most important fact, from the standpoint of this pretreatment investigation, was that all the lignin could eventually be brought into solution, even after 36 hr. of pretreatment.

The Pretreatment of Jack Pine

Thus far the investigation of pretreatment had been confined to a study of spruce wood. In order to determine whether this phenomenon was exhibited by other wood species, a few experiments were made with jack pine wood-meal. A quantity of wood-meal, obtained from the heartwood, was extracted in a Soxhlet extractor with an alcohol-benzene mixture for 24 hr. and then air-dried. Five-gram samples of this extracted wood-meal, and also of the unextracted wood-meal, were cooked in the bronze digesters for three hours at 140° C. The composition of the cooking liquor was:

total SO_2, 5.24; free SO_2, 3.90; combined SO_2, 1.34%. The results of this experiment are compared in Table VIII with those obtained with spruce under the same conditions, and previously reported in Table III.

TABLE VIII

EXTRACTED AND UNEXTRACTED SPRUCE AND JACK PINE WOOD-MEAL, COOKED THREE HOURS AT 140° C.

Wood species	Yield of pulp, %	Carbo- hydrate, %	Lignin in pulp, %	Residual lignin, %	Treatment of sample
Jack pine	53.4	46.0	13.8	7.36	Unextracted
Jack pine	48.4	45.6	3.76	1.86	Extracted
Spruce	48.3	47.0	2.58	1.25	Unextracted
Spruce	49.1	47.9	2.46	1.21	Extracted

NOTE.—*Jack pine wood: density 0.46; lignin content, 32.6%.*

It is evident from the results in Table VIII that unextracted jack pine wood is much more slowly cooked than the extracted wood. Spruce wood, however, can be cooked equally well before extraction and after the resins have been removed. It is interesting to note also, that the solvent-extracted pine is delignified almost as rapidly as the spruce. There is some slight difference in the rates, even when allowance is made for the greater original lignin content of the pine, but this difference might easily be due to the difference in the densities of the two wood species used.

The yields of carbohydrate show a slight difference in favor of the spruce, and a greater difference would be expected if the lignin content of the pine pulp were reduced to that of the spruce pulp.

This experiment confirms Hagglund's (4) assertion that there is no difficulty in delignifying solvent-extracted pine, provided that no water-insoluble extracting fluid-remains within the wood fibres.

Samples of unextracted jack pine wood-meal, and wood-meal extracted with alcohol-benzene for 12 hr., were pretreated in buffer solutions for six hours at 130° C. The samples were then air-dried, and cooked for three hours at 140° C. in sulphite liquor of composition: total SO_2, 5.11; free SO_2, 3.93; combined SO_2, 1.18%. These results are shown in Table IX.

The curves, showing the yields of pulp and the residual lignin plotted against the pH of the pretreating solutions (Fig. 9), are similar to the corresponding curves for spruce, which were shown in a previous paper (3). There is considerable difference, however, in the degree of cooking obtained with the solvent-extracted and unextracted jack pine, and spruce wood-meal. More delignification was obtained in cooking pretreated spruce than was obtained with the solvent-extracted, pretreated jack pine, but there is an almost constant difference between the lignin values for the spruce and solvent-extracted jack pine at any pH below 5. This shows that a change

TABLE IX

SOLVENT-EXTRACTED AND UNEXTRACTED JACK PINE PRETREATED IN BUFFER SOLUTIONS

Pretreating solution, pH	Yield of pulp, %	Carbohydrate, %	Lignin in pulp, %	Residual lignin, %
A. Unextracted wood-meal				
2.2	66.6	42.2	36.6	24.4
3	63.9	44.3	30.7	19.6
4	60.6	45.4	25.0	15.1
5	62.1	46.8	24.6	15.3
6	64.5	48.5	24.6	16.0
8	67.6	49.6	26.6	18.0
B. Solvent-extracted wood-meal				
2.2	63.8	46.1	27.7	17.7
3	58.5	47.1	19.5	11.4
4	53.4	46.6	12.8	6.84
5	53.7	47.5	11.6	6.25
6	57.2	50.2	12.2	6.98
8	62.5	51.2	18.0	11.30
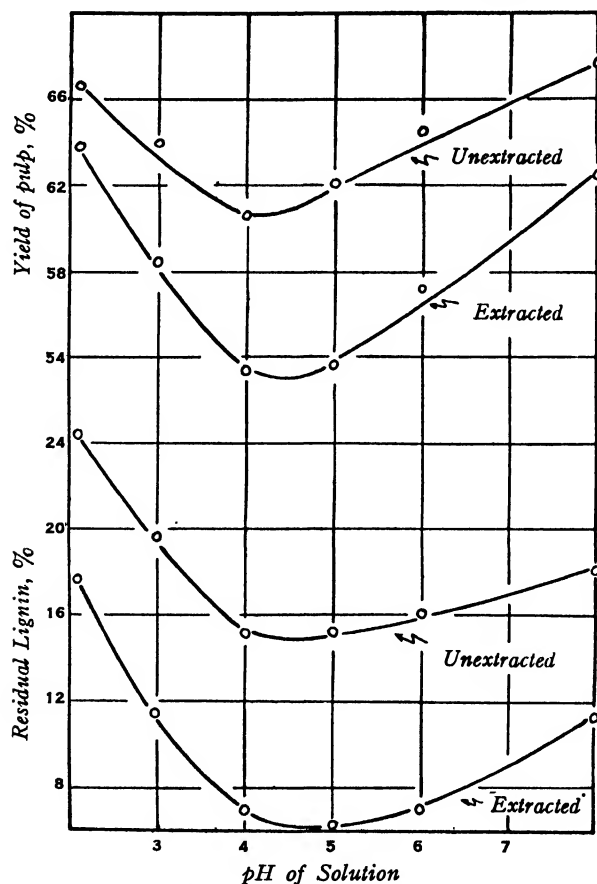
FIG. 9. *Effect of pH of pretreatment at 130° C. for six hours on subsequent delignification of jack pine wood-meal.*

in the hydrogen ion concentration of the pretreating solution had an equal effect on both the spruce and jack pine lignin. The agreement is not so close at pH-values above 5.

The curves also indicate that a change in the hydrogen ion concentration of the pretreating solution does not alter the rate of delignification of unextracted jack pine as much as it does that of extracted jack pine or spruce. A possible explanation for the above results lies in the difference in the rate of penetration of liquids into solvent-extracted and unextracted pine wood. De Montigny (6) found that some substances existed in jack pine which hindered the penetration of liquids into the wood. When these substances were removed, by extracting the chip with organic solvents, the rate of penetration was greatly increased. The presence of resins, fats, and waxes in the wood fibres may hinder the diffusion of the buffer solution to the lignin surface, and also the diffusion of the cooking liquor. If this were true, the acids formed in the fibres during pretreatment would have considerable effect in determining the hydrogen ion concentration in contact with the lignin particles, and would modify the influence of the buffer solutions. This factor would have a more noticeable effect the more the pH of the buffer solution differed from that due to the acids formed in the wood, and the lignin curve would rise less steeply on either side of the minimum.

Since the minimum in the pretreatment curves for both spruce and jack pine occurs at the same pH, there appears to be no fundamental difference between spruce and jack pine lignin. The curves for the jack pine are merely displaced upward, owing to a slower rate of cooking, which might easily be explained by differences in the wood structure, and the nature and quantity of the resins in the two wood species.

Discussion

Reference has already been made to the hypothesis that lignin may coagulate when heated in aqueous media, and that this tendency of the lignin to coagulate may exert considerable influence during the normal cooking process. The writers of course realize the possibility of the alternative hypothesis that the lignin may be altered chemically during pretreatment in such a way that subsequent cooking is rendered more difficult. At this point it is therefore desirable to assemble the salient facts for a general consideration, and to discuss their relation to the hypotheses mentioned above.

It has been demonstrated that when wood is heated in aqueous media it becomes very difficult to delignify in bisulphite solutions. The hypothesis has been advanced that the lignin, existing in the wood as submicroscopic particles, or even as thin films upon the cellulose fibres, may tend to agglomerate under these conditions to form a smaller number of relatively larger particles. Such a coagulation would result in a great decrease in the lignin surface, and, since the lignin is in the solid phase, the reaction with solvent solutions might be confined to this surface. The rate of the reaction would thus be decreased.

The fact that the rate of delignification of wood in sulphite liquor approximately obeys the law of a first order reaction, in spite of all the variable factors concerned, is difficult to explain on the basis of chemical reactions. One would expect the rate to increase beyond that given by a first order reaction as sulphonation becomes more complete, and also that the liberation of acids into the solution would increase the rate of hydrolysis. The conception of a tendency for the lignin particles to coagulate, and thus oppose the cooking action, which tends to decrease the size of the lignin particles, offers a ready explanation for the nearly straight line relation observed. Further, the curves of rate of delignification (see Fig. 8) of pretreated wood are of the shape one would expect on the basis of the above considerations. Thus, if the lignin particles are considered to have been coagulated by the preliminary treatment, a gradual increase in the cooking rate, such as was observed, would be expected as the particles become smaller in size owing to the cooking reaction. The reaction at the surface of these particles would finally reduce them to a size comparable to that of the lignin particles which are present in an ordinary cook, and the rate of pulping should then be the same as in cooking untreated wood. The curves in Fig. 8 illustrate this point, for after about 12 hr. of digestion the rate curve for the pretreated wood becomes virtually parallel with the curve for the untreated wood.

A coagulation of the lignin particles might affect the cooking rate in two ways; namely, by decreasing the rate of sulphonation, and by decreasing the rate of hydrolysis. The rate of sulphonation has been proved to be decreased by heating wood in aqueous solutions, and there is evidence that the rate of hydrolysis is also decreased. This is indicated by the logarithmic curves of the delignification rates for pretreated and untreated wood (Fig. 8). After one hour of cooking the sulphur value, as percentage of lignin, for the untreated wood, is equal to the sulphur value obtained after six hours of cooking with the pretreated wood: namely, 4.81%. The slopes of the two curves, however, are vastly different at these points, the rate of delignification being much less in the case of the pretreated wood. It is possible that, in the case of the pretreated wood, all the sulphur may not be taken up in such a manner as to assist in the dissolving of the lignin, but there is no reason to believe this to be true, whereas a decrease in the rate of hydrolysis would appear to be the logical consequence of a decrease in the exposed surface of lignin.

Calhoun and Maass (1) have found evidence that the effect of neutral salts in the pretreating solution is in the order of the lyotropic series for the swelling of wood. This suggests that the loosening of the wood structure by swelling may allow the lignin particles a greater mobility, and hence increase the ease with which a number of particles may gather together to form one large particle. Swelling may thus be involved in the pretreatment of wood in buffer solutions. Little is known about the effect of pH on the swelling of wood at high temperatures, although pH has no effect on the swelling of wood at room temperature except in very alkaline solutions (9).

The minimum in the curve of pH of pretreatment may, however, be due to some entirely different cause, either from the standpoint of a physical or a chemical change in the lignin. And the fact that a minimum is obtained does not provide much evidence in favor of either hypothesis. Similarly, the effect upon the rate of delignification of increasing the temperature or the time of pretreatment can be explained equally well as a chemical polymerization, or as a physical coagulation of the lignin particles. It should be emphasized, in this respect, that the physical process cannot be considered as gel formation, which takes place when the temperature is lowered, for the lignin particles are already in the form of a gel, but the heating of lignin in aqueous solutions might cause coagulation somewhat analogous to the coagulation of albumin under the influence of heat. The time and temperature of pretreatment might also control the extent of the coagulation, through determining the mobility of the lignin particles. Any factor that tends to loosen the wood structure would be expected to allow the particles greater freedom of movement.

If the effect of pretreatment is a chemical polymerization that blocks the group to which the bisulphite ion adds, the process must be considered reversible. Such a process is possible, but does not lend itself so readily to an explanation of all the experimental results. Thus far the greater part of the evidence seems to favor a colloidal change that leaves the lignin unaltered chemically, inasmuch as it can be completely dissolved by the action of sulphite liquor, although at a reduced rate of pulping. Some chemical change, however, is a definite possibility that should not be ignored, and further investigation of the problem may reveal definite evidence in favor of such a change.

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STUDIES OF CARBON BLACK

IV. THE CHANNEL PROCESS—THE EFFECT OF DRAFT CONTROL AND CHANNEL HEIGHT ON RUBBER REINFORCEMENT, SORPTION, AND VOLATILE CONTENT[1]

By L. M. PIDGEON[2]

Abstract

In an experimental carbon black plant of the channel type, the effect of channel height, draft control and gas composition on the properties of the carbon has been examined. The channel height was shown to be the most important variable. The rubber reinforcement and the yield of the carbon vary in a similar manner with the channel height at which the carbon was recovered. The sorption of the iodine and methylene blue increased almost logarithmically with the channel height. No direct relation between reinforcement and sorption is possible over the whole range, although the very high sorption obtained at greater channel heights was accompanied by a retarded cure. Sorption was increased by heating the blacks. The volatile content is high at low channel heights, passing through a minimum at the point of optimum yield. This test showed even poorer correlation with rubber reinforcement. Apparent density varied directly with channel height.

The effect of draft control upon reinforcement, sorption, and volatile content was indefinite. However, the volatile content seemed to vary directly with the yield. No effects characteristic of the gas composition were found.

Introduction

The properties of the carbon black from a given plant are known to be subject to daily and even hourly variations, the causes of which are either unknown or beyond the control of the operator. One of the chief reasons for the persistence of this condition is the lack of a convenient and characteristic test to evaluate and specify the properties of carbon black. The only test of quality that is satisfactory to the rubber industry consists of actually incorporating the carbon in rubber, using a test formula, followed by vulcanization and examination of the tensile properties of the resultant rubber stock. This procedure is too slow and cumbersome to be well suited to plant control.

Many attempts have been made to correlate the reinforcing action of pigments with other characteristics that are more readily measurable. Some of these tests, chiefly those concerning sorptive power and volatile content, have shown some measure of success. Where correlation has been found, however, it has been in cases where obvious differences in behavior already

existed, such as those appearing between the broad classes of carbons. Very little information is available that correlates these tests with the rubber test and at the same time relates them to the known and controllable variables of production, such as the distance between the burner tip and depositing surface, and the restriction of draft. Until the effect of these known variables has been established, few improvements in production control can be achieved by the application of various tests to channel blacks that differ from one another for reasons unknown.

Plummer and Keller (14) examined the rubber reinforcement and iodine sorption of samples produced from propane in an experimental plant, but none of the controllable variables appeared to affect the properties of the black, unless very wide changes in operating conditions were involved. In the present work the channel height has been found to exert a very definite effect on the sorptive capacity and rubber reinforcement of the carbon.

The production of carbon black in an experimental channel apparatus was dealt with in previous papers of this series (12, 13), and the effect, on the recovery of carbon, of changes in the channel height and the draft control was examined. Both natural gas and synthetic gases containing olefines in various concentrations were employed. The production of many samples of known history presented an opportunity to examine the effect of these variables of production on the vulcanization characteristics, sorptive capacity, and volatile content of the carbons.

Reinforcement of Rubber

The carbon black samples were produced in the experimental channel apparatus that has been described previously. The effect upon yield of varying the controllable factors of production has been described in detail in previous papers of this series.

After removal from the apparatus the samples were brushed through a 100 mesh screen to break up lumps and remove any large particles. Owing to the fact that the channel used in these experiments had been ground, the scrapers were very efficient and practically no grit appeared in any of the samples.

Carbon black samples were incorporated into rubber on an open mill, using the standard diphenyl guanidine test formula described in the first paper of this series (11) (smoked sheet, 100; zinc oxide, 3; sulphur, 5; stearic acid, 2; D.P.G., 0.75; carbon, 35). The resulting compound was vulcanized in a four-cavity mold heated in a steam press to 141.5° C. for the times indicated in the tables. Tensile tests were made by two operators with dumbbell pieces in the usual manner.

Effect of Channel Height

It has been shown that the recovery of carbon from any given flame is directly dependent on the channel height, a fairly sharp maximum existing for any given flame. The tensile properties of rubber stocks containing carbon

TABLE I
EFFECT OF CHANNEL HEIGHT ON YIELD AND RUBBER REINFORCEMENT

Sample	Channel height, in.	Yield, lb. per 1000 cu ft.	Modulus at 300% elongation, kg. per sq. cm.				Modulus at 500% elongation, kg. per sq. cm.				T_B, kg. per sq. cm.				E_B, %				Hardness, (Shore)			
Cure time, min. →			65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125
A. Pyrolysis waste gas. Cabot tip, 0.022 in.																						
C29	1.92	3.3	73.3	89.2	94.6	93.7	191	219	247	233	249	291	296	277	583	590	560	560	59	61	64	65
C17	2.44	4.4	91.2	104	110	107	220	243	253	243	306	302	290	262	608	570	540	518	59	61	64	65
C18	2.84	3.9	77.8	93.7	99	108	193	225	232	244	281	296	304	285	650	628	623	580	57	60	62	63
C19	3.20	3.4	77.4	91	100	100	196	219	228	225	259	285	268	247	590	583	550	533	58	62	63	63
C21	3.61	2.2	61.4	72.7	80.2	85.2	154	182	194	204	191	210	228	234	567	547	548	547	56	58	60	60
B. Propane-butane (70 : 30). Cabot tip, 0.012 in.																						
C35	1.24	2.3	51.0	57.8	65.0	65.8	128	147	159	157	207	230	243	236	612	620	610	607	54	55	61	61
C36	1.64	2.8	52.0	59.0	58.9	65.0	136	152	153	159	240	243	258	251	640	630	640	607	56	57	56	61
C37	2.04	3.6	57.8	61.0	76.0	77.6	154	179	190	187	239	269	274	276	625	622	603	612	54	55	56	58
C42	2.44	4.9	93.0	100	114	125	234	253	285	292	300	312	325	305	595	575	552	516	59	61	62	64
C41	2.84	3.8	71.0	80.4	93.2	102	192	213	233	247	278	300	312	308	609	607	585	587	57	57	60	63
C39	3.24	2.2	50.0	63.0	75.8	83.0	141	168	193	207	181	228	242	255	575	589	563	561	52	57	58	61
C40	3.64	1.1	40.5	47.3	56.5	66.1	117	135	162	175	167	185	205	236	578	586	566	585	51	52	55	58
C. Propane-butane (70 : 30). Cabot tip, 0.022 in.																						
C31	2.44	3.0	67.1	76.6	81.0	84.0	177	193	202	215	237	240	238	247	600	590	550	560	55	57	59	59
C32	2.84	3.9	71.6	83.0	90.0	90.0	185	206	220	220	265	277	271	265	615	600	570	565	56	58	59	59
C33	3.20	4.3	74.0	85.0	92.8	97.0	194	204	224	237	255	274	263	261	600	595	540	520	56	58	59	60
C34	3.64	3.9	66.3	77.0	87.0	89.0	177	219	219	223	252	272	290	286	590	610	595	570	54	55	57	58
C46	4.40	2.3	51.6	65.8	74.2	73.2	135	163	185	187	155	193	202	201	510	525	540	515	52	56	57	57

blacks prepared at various channel heights are shown in Table I and in Fig. 1. A very definite relation exists between stiffness and ultimate tensile strength and the channel height at which the carbon was produced. The point of maximum reinforcement corresponds approximately to the channel height at which the recovery of carbon is the greatest, so that a plot of yield against rubber reinforcement is a straight line, as can be seen in Fig. 2.
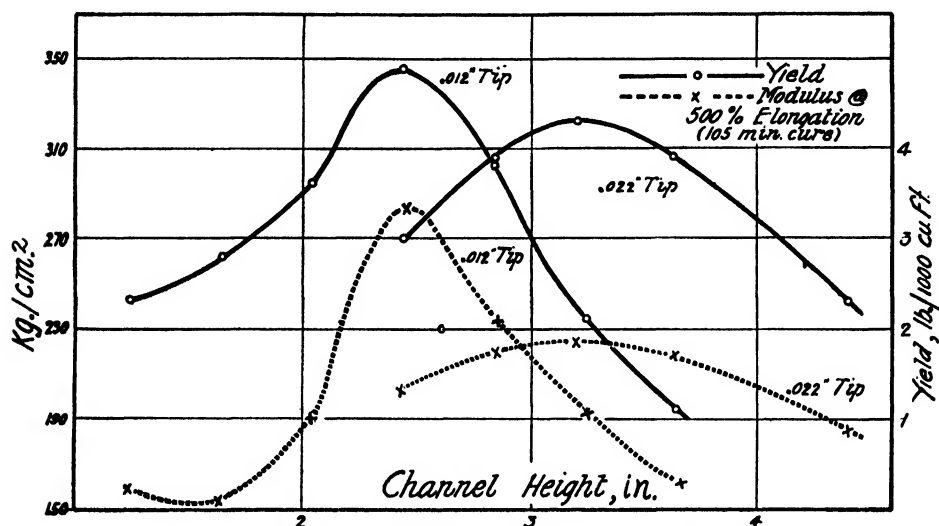
FIG. 1.   *Relation between rubber reinforcement, yield and channel height.   Carbon black from 70:30 propane-butane.*
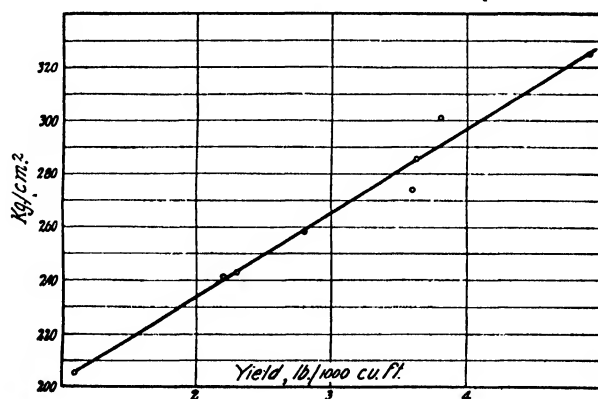
FIG. 2.   *Relation between yield and tensile strength (cure time, 105 min.).*

Table I includes the results obtained with two gas mixtures and with two burner tips, and while the maxima appear at different positions, the relation between channel height and stiffness is similar in every case. (It should be noted that the results in Section *A* of Table I were obtained with a sample of raw rubber different from that used in Sections *B* and *C*.)

At great channel heights the cure was strongly retarded, so that the optimum tensile strength was not attained in the maximum cure time of 125 min. With lesser channel heights there does not seem to be much difference in the time of cure, as can be seen in Fig. 3, in which the ultimate tensile strength
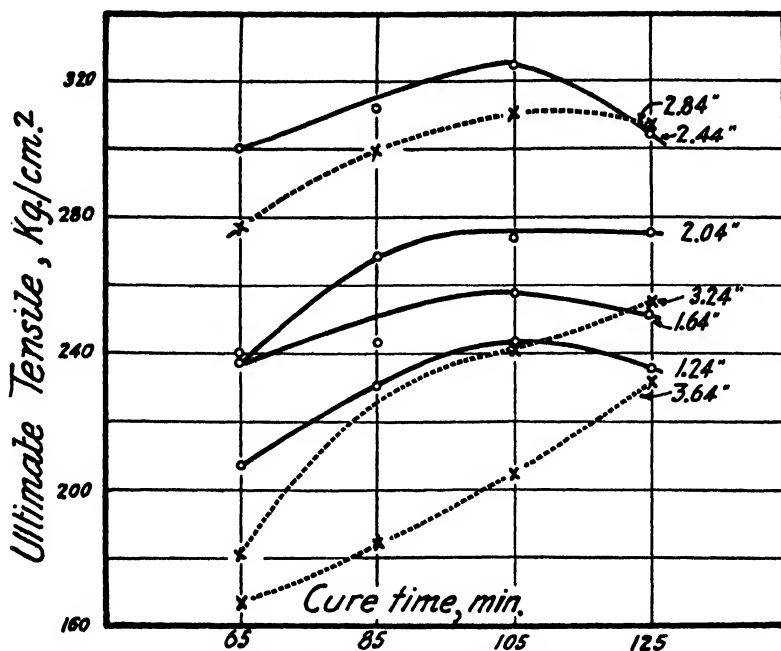
FIG. 3.   *Effect of channel height on rubber reinforcement.*

is plotted against cure time.   The curves pass through a maximum at a channel height of 2.44 in., and all except the greatest channel heights show maxima in the vicinity of 105 min. cure.   The work of Plummer and Keller (14) gave no conclusive information on a relation of reinforcement to channel height, as only three channel heights were reported, but it appeared that the optimum tensile properties coincided with optimum yield.

Effect of Draft Control

It has been shown previously that the yield may be increased if restriction of the air supply in the burner chamber causes a steady burning of the flames. With unrestricted draft, convection currents cause the flames to flicker and consequently cause the yield to fall.   Moderate restriction of draft improves this condition and increases the recovery of carbon.   Restriction to the limit tolerated by the flame reduces the luminosity and greatly reduces the carbon recovery.

The results shown in Table II were obtained with carbon that was produced from pyrolysis waste gases.   During the production of these samples the flames flickered excessively when the draft was unrestricted. The yield was increased when the drafts were closed.   The reinforcing power of the carbons

TABLE II

Eff OF DRAFT CONTROL ON RUBBER RE

Sample	Upper draft aperture	Yield, lb. per 1000 cu. ft.	Carbon dioxide	Oxygen	Modulus at 300% elongation, kg. per sq. cm.				Modulus at 500% elongation, kg. per sq. cm.				T_B, kg. per sq. cm.				E_B, %				Hardness, (Shore)			
					65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125
C22	100	3.1	1.0	19.2	74.2	89.4	98.4	101	199	218	235	235	268	279	290	278	598	568	565	537	56	63	64	62
C23	50	3.2	1.5	17.2	72.1	85.6	94.6	97.5	183	212	222	224	245	271	291	284	600	575	590	588	57	61	60	64
C24	38	3.5	1.8	16.3	76.2	92.0	101	102	194	224	249	242	274	300	311	290	608	598	590	558	60	61	61	64
C18	27	3.9			77.8	93.7	98.8	108	194	225	252	244	310	319	312	328	652	625	607	597	60	61	62	64
C25	21	3.5	3.5	14.1	83.6	98.0	102	99.5	210	242	249	238	258	321	313	306	563	598	583	578	60	64	61	57

Pyroly: off-g

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TABLE III

RUBBER REINFORCEMENT BY COMMERCIAL SAMPLES

Commercial sample	Modulus at 300% elongation, kg. per sq. cm.				Modulus at 500% elongation, kg. per sq. cm.				T_B, kg. per sq. cm.				E_B, %				Hardness, (Shore)			
	65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125	65	85	105	125
A	62.2	78.3	85.6	96.4	161	195	210	222	228	271	285	280	608	609	605	580	56	58	61	61
B	56.5	75.0	79.8	88.5	153	185	199	215	235	272	276	280	625	620	605	585	55	56	61	61
C	58.2	73.7	79.1	87.3	153	188	196	211	234	270	279	278	630	610	618	590	56	59	61	63

again follows the yield, passing through a maximum at approximately the same draft setting. The differences are rather small, however, and suggest that, as in the case of the yield, the draft control is a secondary factor.

Speed of Channel Motion

Drogin (5) has mentioned that the amount of heating to which the carbon is subjected will affect its color and even the rate of cure in a rubber mix. In the channel process the carbon is deposited in successive layers which continue to be built up until removal by the scraper. In large-scale practice, any given section of the channel moves across a number (10 to 20) of burners before passing over a scraper. It might be expected that the thickness of this layer would play an important part in the recovery and quality of the carbon, since, owing to the excellent insulating properties of carbon black, it will affect the temperature of deposition and the temperature of the channel in any given apparatus. In the experimental plant the number of flames playing on any given section of the channel is much smaller than in full-scale practice, but by reducing the speed of channel motion it is possible to produce a relatively thick layer of carbon before it is removed by the scraper.

The effect of channel speed on the properties of the carbon is shown in Table IV. In spite of the different conditions under which these samples were obtained, very little difference in their rubber reinforcement is observed.

TABLE IV

EFFECT OF CHANNEL SPEED

Sample	Channel speed, in. per min.	Modulus at 500% elongation, kg. per sq. cm.				T_B, kg. per sq. cm.				E_B, %			
Cure time, min.→		65	85	105	125	65	85	105	125	65	85	105	125
C 26	2.9	204	229	241	243	302	303	302	296	633	605	578	567
C 18	1.8	194	225	232	244	310	319	312	328	652	625	607	597
C 27	0.9	215	245	242	237	295	316	302	287	618	598	573	560

Pyrolysis waste gas. Channel height, 2.84 in. Draft, 27%.

Effect of Gas Composition

It will be observed that rubber tests have been carried out with carbon blacks produced by the partial combustion of paraffin gases and gases containing fairly large proportions of olefines and hydrogen. No important difference between either the magnitude of the results or their general trend has been observed.

In Table III the results of rubber tests of certain standard commercial rubber blacks are shown. The reinforcement is in all cases similar to that produced by the average sample of experimental black, and somewhat inferior to the best.

Sorption

The sorptive power of a finely divided solid affords one of the most useful tests with which to describe and specify the properties of the substance. The amount of any sorbate which will be taken up depends obviously on (i) an intensity factor, which represents the actual affinity between a given surface and the sorbate; and (ii) a capacity factor, which indicates the amount of surface available or, in other words, the shape and size of particle. Both of these factors are concerned in the reinforcing power of carbon black, and the dominant position that this filler has rapidly assumed in the rubber industry is due to both (i) and (ii). The particle size is smaller than that of any other known filler, while the "affinity" or "bond" between carbon black and rubber must be such as almost to suggest the formation of a carbon-carbon bond with rubber. (Lithopone, for example, of reasonably small particle size, exerts little reinforcing action, owing presumably to poor "affinity".) These factors are measured simultaneously when the sorptive power of a carbon black is determined, and, in fact, it is almost impossible to separate them by this test alone.

Other ingredients of a rubber compound may be adsorbed by carbon black because the carbon black presents a large surface for sorption. When ingredients thus adsorbed include the accelerator, or other agents essential to the vulcanization reaction, a retardation of cure results.

Many attempts have been made to relate the cure time with the sorptive power of the carbon, because a direct correlation would be of inestimable value to the rubber chemist. A survey of the literature soon shows that the results have not been promising. Fromandi (6) examined the sorption of acetic acid and could find no correlation with vulcanization characteristics. Spear and Moore (16) found no basic relations between the stiffness of a rubber stock and the sorption of acid or basic dyes. Ditmar and Preusse (3) and Goodwin and Park (7) found a retarding effect when sorption was high, and suggested removal of sulphur or some other essential constituent of the vulcanization reaction as the cause.

Wiegand and Snyder (20), Drogin (4), and Amon and Estelow (1) assumed that the retardation is due to accelerator sorption; they used the sorption of diphenyl guanidine as the basis of a test. In most cases it was found that a sorption test readily separated and distinguished the broad classes of carbon black, but was barely able to distinguish between individual members of a group.

A puzzling phenomenon was observed by Carson and Sebrell (2) who found that blacks that had been heated to 900° C. exhibited increased sorption accompanied by a more rapid curing rate. (Wiegand (17) has obtained a patent covering the heating of black to accelerate the cure, but his specification also states that the sorptive power is reduced.) More recently Schoenfeld (15) has suggested that the sorption by carbon black may be of the activated type. His results indicate that certain acidic impurities present ordinarily in carbon black inhibit the cure, and their removal at high temperatures results in more rapid cure, even though the sorptive power is enhanced.

In most of the work that has been carried out on this subject, it has been customary to select a certain number of samples known to differ in vulcanization characteristics, and to attempt to find similar differences in the sorptive power. The actual samples were unrelated and frequently obtained from various sources, while the differences in details of production responsible for the measured differences in vulcanization characteristics were generally unknown. The author has been able to produce a series of samples, the rubber reinforcement of which varies in a regular manner and is related to the conditions under which the samples were produced. An opportunity was therefore offered to examine the relation between reinforcement and sorption under such circumstances that the existence of any correlation could be readily detected.

Previous workers have employed organic accelerators, dyes, acids, alkalis, and even water itself to determine the sorptive power of carbon black. Iodine and methylene blue have been chosen in this research since they may be readily estimated in solution, and represent such widely different types of molecule that any relation appearing in both cases may be considered to be a general sorption phenomenon and not a reaction peculiar to any given sorbent and sorbate.

Methylene Blue

The sample of carbon black was shaken for one hour with 0.025% aqueous solution of methylene blue. (Times up to three hours gave similar results.) In the standard test 0.25 gm. of sample in 50 cc. of solution was used, but other concentrations were also employed to determine the sorption isotherm. The concentration of the subsequent solution was measured colorimetrically after separation of the carbon black. Centrifuging and filtration were both employed; similar results are obtainable with both methods if precautions are taken to ensure that the filter paper is saturated with dye at a concentration that is in equilibrium with that of the filtrate. In practice the colorimetric determination was carried out on successive fractions until constant readings were obtained.

Iodine

Carbon (0.25 gm.) was shaken for 30 min. with 50 cc. of 0.01 N iodine-potassium iodide solution in a glass-stoppered bottle. The mixture was then centrifuged and 10 cc. of the clear supernatant liquid titrated with 0.01 N thiosulphate. The amount of sorption was calculated from the concentration of the final solution.

Sorption Index

In most of the work done on sorption by carbon black it has been customary to submit the samples to some standard test similar to those described. That is, the sorption isotherm showing the amount sorbed when the carbon is in equilibrium with solutions of various concentrations was not fully determined.

Since the isotherms for a number of closely related samples are likely to be affine, this procedure is justifiable, but a serious error is frequently introduced by neglecting to compare the amounts of sorption at the same final concentration. Samples of higher sorptive power will produce more dilute solutions which in turn prevents them from showing the full extent of their sorptive capacity. Goodwin and Park (7) overcame this difficulty by adjusting the volume of the solution to compensate for the differences in sorptive power, so that a standard end point was produced in every case. This method, while capable of considerable accuracy, is cumbersome, owing to the time required to attain equilibrium after alteration of the concentration of the solution.

A basis for comparison has been obtained by dividing the amount of sorption in milligrams per gram of black by the concentration of the final solution. Thus a sample of high sorption will have its $\frac{x}{m}$ divided by a number corresponding to a low concentration. The result is termed the "sorption index" and offers a convenient means of compensating for the discrepancies in final concentration when the sorption characteristics of the carbon are measured by means of a single determination at one concentration.

Effect of Channel Height on Sorption

The sorption of methylene blue by samples produced from methane and various other hydrocarbon gases is shown in Tables V and VI. In every case the amount of sorption increased with increase in channel height. The relation is approximately logarithmic, and at the greatest channel heights very high values of sorption are attained. (At this point the sorptive power is still very much inferior to that of a good decolorizing carbon, which gives

TABLE V

EFFECT OF CHANNEL HEIGHT ON SORPTION OF METHYLENE BLUE

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	x/m, mg. dye per gm. of carbon	Sorption index
A. Carbon black from Turner Valley gas. (For details see Reference (12))				
Cabot, 0.10 in. slot: rate, 2.46 cu ft. per hr.				
20	1.25	0.7	26.2	2.3
21	1.50	1.2	31.9	3.3
15	1.75	1.3	37.5	5.9
19	2.00	0.7	44.8	17.2
23	2.25	0.3	46.2	24.6
B. CH₄, 85; C₂H₆, 13.5; N₂, 1.5%. Cabot, 0.022 in. slot: rate, 4.6 cu ft. per hr.				
1	1.50	0.4	32.4	3.7
2	1.75	0.6	35.6	5.0
3	2.00	1.0	41.2	9.3
4	2.25	1.1	42.0	10.5
5	2.50	0.9	47.5	39.5
6	2.75	0.7	48.8	81.3

TABLE VI

Relation between sorption and rubber reinforcement

A. Carbon black from propane-butane (70 : 30) (for production details see Reference (13))

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	x/m, mg. methylene blue per gm. of carbon	Sorption index	Modulus at 500% elongation	T_B, kg. per sq. cm.
C36	1.64	2.8	16.8	1.0	258	153
C37	2.04	3.6	20.8	1.4	274	190
C38	2.44	4.9	25.2	2.0	325	285
C41	2.84	3.8	37.6	5.9	312	233
C39	3.20	2.2	40.0	8.0	242	193
C40	3.64	1.1	47.6	39.6	205	162

B. Carbon from pyrolysis off-gas: C_2H_2, 1.2; C_2H_4, 23.0; C_3H_6, 11.0; H_2, 14.8; C_nH_{2n+2}, 50.0% (n = 1.1)

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation	T_B, kg. per sq. cm.	x/m, mg. methylene blue per gm. of carbon	Sorption index	x/m, mg. iodine per gm. of carbon	Sorption index
C29	1.92	3.3	247	296	30.8	3.2	90.8	1.2
C17	2.44	4.4	253	290	36.8	5.6	104.0	1.5
C18	2.84	3.9	232	304	37.6	6.1	116.4	1.8
C19	3.20	3.4	228	268	41.6	9.7	128.8	2.3
C21	3.61	2.2	194	228	46.6	21.2	142.4	2.9

Cure time, 105 min.

an index of infinity by the standard test.) While the magnitude of the values are different, the relation between channel height and sorption is similar in all cases, as shown also in Fig. 4. (Carbon produced from methane appears to be a more active sorbent than that from "richer gases".) The same order is obtained when iodine is used, so that the relation between channel height and sorption may be regarded as a general one.

While the author is unaware of any other published work in which a similar relation has been described, it is of interest to note that Wiegand (18) states that the black deposited on the centre of the channel shows lower sorption than that deposited near the edges. This centre position, which is, of course, nearer to the burner tip, corresponds to a lower channel height than does the edge.

It has been pointed out previously in this series that particles of smallest size are likely to be produced when the temperature of the "cracking" zone is very high and the time of contact correspondingly short. Casual inspection of the flame will indicate that this condition is achieved at relatively high channel settings when the flame is less cooled by the channel. Quantitative measurements of this effect are being made and will be reported subsequently.
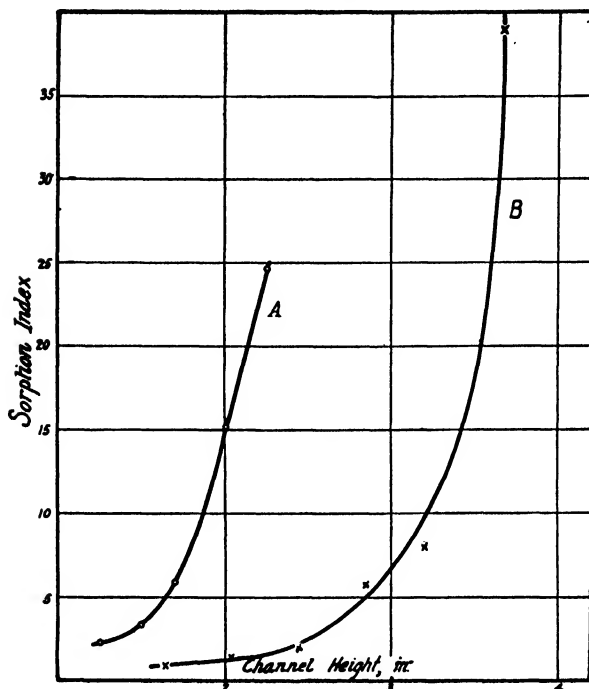
FIG. 4. *Relation between channel height and sorption. A, carbon black from Turner Valley gas (15). B, carbon black from 70:30 propane-butane.*

Relation Between Sorption and Rubber Reinforcement

It has been shown that the reinforcement by a series of carbon blacks passes through a maximum as the channel height at which they are produced passes from a minimum to a maximum, being relatively poor at the lowest and highest channel heights employed. Comparison of this behavior with sorption (Table VI) indicates that, considering the whole range of channel heights, no correlation exists between the tests. For example, the carbon obtained with a channel height of 2.84 in. produced an ultimate tensile strength of 312 kg. per sq. cm., and showed a corresponding sorption index of 5.9. The sample obtained at 2.04 in. broke at 274 kg. per sq. cm. and had a lower sorption index, 1.4.

The test is not completely useless, however, since the sorption at very great channel heights was very much greater and the corresponding rubber test showed strongly retarded cures. A direct relation existed between sorption and stiffness for any given cure time, in the case of blacks produced from pyrolysis off-gas, between the channel setting productive of maximum yield and the greatest setting employed.

These results show clearly why the sorption test is of limited use when applied to ordinary channel blacks. Commercial rubber blacks are likely to be made at channel settings that produce the optimum yield, and the variations that take place are probably due to changes in the effective channel

height brought about by atmospheric disturbances or fluctuations in gas pressure, both of which affect flame size, and, therefore, alter the relative position of the depositing surface. Rubber reinforcement falls off on either side of the optimum channel height, while sorption increases continuously in intensity as the channel height is increased. It is possible, therefore, to find two samples showing identical reinforcement yet varying widely in sorptive capacity. On the other hand, while a sample showing low sorption may not necessarily exhibit good rubber properties, very high sorption is almost certainly an indication of cure retardation.

Effect of Draft Control

It has been shown that the differences in draft control that may be brought about in the experimental apparatus have very little effect on the rubber properties of the carbon. A small regular difference in sorption is noticed, the direction being such that sorption increases slightly with draft restriction, and falls off again at the highest restriction possible. This effect is clearly shown in Tables VII and VIII.

In view of the large differences in sorptive power which may exist without corresponding differences in rubber reinforcement, it may be said that draft control has no significant effect on sorption.

TABLE VII

EFFECT OF DRAFT CONTROL ON SORPTION

Sample	Draft aperture	x/m, mg. methylene blue per gm. of carbon	Sorption index
0.010 in. slot			
52	100	42.0	10.5
53	50	44.9	17.9
56	38	46.4	25.8
60	21	40.0	8.0
0.012 in. slot			
15	100	37.5	5.9
24	79	41.2	9.4
25	50	41.2	9.4
26	30	41.2	9.4
16	21	33.6	4.5

Carbon from Turner Valley gas; channel height, 1.75 in.

TABLE VIII

EFFECT OF DRAFT CONTROL ON SORPTION

Sample	Draft aperture	Flue gas		x/m, mg. methylene blue per gm. of carbon	Sorption index	x/m, mg. iodine per gm. of carbon	Sorption index	T_B, kg. per sq. cm.	Modulus at 500% elongation
		Carbon dioxide	Oxygen						
C22	100	1.0	19.2	38.8	6.9	105.6	1.6	290	235
C23	50	1.5	17.2	39.4	7.4	121.6	2.0	291	222
C24	38	1.8	16.3	39.6	7.6	116.4	1.9	311	249
Bulk	27	–	–	37.4	5.9	116.4	1.9	312	232
C25	21	3.5	14.1	37.4	5.9	100.0	1.4	313	249

Carbon from pyrolysis off-gas (composition as in Table VI, B). Cabot tip, 0.022 in. slot; rate, 6.0 cu ft. per hr.; channel height, 2.84 in.; cure time, 105 min.

Effect of Channel Speed

Rubber reinforcement is little affected by the speed at which the channel moves in the experimental plant, while sorption is slightly increased by the continued heating which results from a slow moving channel, as shown in Table XI. In view of what has gone before, these differences may be regarded as negligible.

TABLE IX

EFFECT OF CHANNEL SPEED ON SORPTION

Sample	Channel speed, in. per min.	Modulus at 500% elongation, kg. per sq. cm.	T_B, kg. per sq. cm.	x/m, mg. iodine per gm. of carbon	Sorption index
C26	2.9	241	302	116.4	1.9
C18	1.8	232	312	116.4	1.9
C27	0.9	242	302	124.4	2.2

Pyrolysis waste gas; channel height, 2.84 in.; cure time, 105 min.

Miscellaneous Blacks

For purposes of comparison a number of standard commercial carbon blacks have been examined. The results are shown in Table X. The sorption test gives no useful information, since the differences between the blacks are too small to be of significance. The thermatomic carbon, "Thermax", shows very little sorption, a fact already well known (7). The commercial

TABLE X

SORPTION BY VARIOUS CARBON BLACKS

Sample	x/m, mg. methylene blue per gm. of carbon	Sorption index	x/m, mg. iodine per gm. of carbon	Sorption index	T_B, kg. per sq. cm.	Modulus at 500% elongation, kg. per sq. cm.
Commercial B	33.6	4.7	100.8	1.4	285	210
Commercial A	32.0	3.6	97.2	1.3	279	196
Thermax	9.2	0.5	21.2	0.2	215	159

Cure time, 105 min.

blacks show sorption values that are very similar to those of the best experimental blacks obtained in this research, but as is shown in Table II, their rubber reinforcement is somewhat inferior.

Effect of Gas Composition on Sorption

Carbon black has been produced from a number of hydrocarbon gases and from mixtures of gases, as described previously, and the sorptive properties of a number of these carbons have been examined. The results, shown in Table XI, fail to indicate a relation between sorption and the composition of the gas supplied to the flame. Any differences that appear are probably

TABLE XI

EFFECT OF GAS COMPOSITION

Ethylene	Methane	Hydrogen	Yield, lb. per 1000 cu. ft.	x/m, mg. methylene blue per gm. of carbon	Sorption index
100	–	–	4.3	35.6	4.9
90	–	10	4.2	37.6	6.0
85	–	15	3.4	35.6	4.9
10	90	–	1.7	34.4	4.4
25	75	–	2.0	30.0	3.0
–	90	10	0.8	36.0	6.0
–	100	–	1.3	37.5	5.9

Cabot, 0.012 in. slot; gas rate, 2.7 cu. ft. per hr.; channel height, 1.75 in.; upper draft, 21.0% open.

due to changes in the height of the flame which, owing to greater spreading over the channel, has the effect of altering the effective distance of the depositing surface. The similarity in sorption index is rather striking in view of the large differences in yield, which means that the amount of carbon deposited per unit of time was different in each case.

Effect of Heating on Sorption

A number of samples were heated to 950° C. *in vacuo* for seven minutes and then their sorptive power was measured. The results are shown in Table XII, where it will be seen that in almost every case the sorptive power

TABLE XII

EFFECT OF HEATING ON SORPTION AT 950° C. *in vacuo*

Sample	Methylene blue			Iodine		
	x/m, mg. per gm. of carbon	Sorption index	Sorption index (unheated)	x/m, mg. per gm. of carbon	Sorption index	Sorption index (unheated)
C29	38.0	6.3	3.1	175.2	5.3	1.2
C17	39.6	7.6	5.6	145.2	2.5	1.5
C18	40.8	8.9	6.0	195.2	8.6	1.8
C20	44.8	17.2	11.2	180.4	6.0	2.4
C21	45.6	21.0	21.2			
C23	39.6	7.6	7.4			
C24	38.0	6.3	7.6			
C25	34.0	4.2	5.9			

of the sample has been increased by heating. This supports the findings of Carson and Sebrell (2). The increase in sorption was much more marked with iodine than with methylene blue, a fact that may be connected with the difference in size of these molecules. Methylene blue, owing to larger molecular dimensions, may be less able than iodine to avail itself of the increased surface formed by removal of volatile matter.

The increase of sorption follows the removal of volatile matter at various temperatures, as shown in Table XIII. A number of determinations were made at successively higher temperatures. The increase of sorption depends on the removal of volatile matter, and becomes particularly noticeable at 1000° C. Such temperatures are of the same order of magnitude as those employed in the activation of charcoal, where it was found that temperatures up to 1100° C. may be used with advantage.

TABLE XIII

EFFECT ON SORPTION OF HEATING COMMERCIAL CARBON BLACK C AT VARIOUS TEMPERATURES

Temp., °C.	Volatile loss, %	x/m, methylene blue per gm. of carbon	Sorption index
20	–	38.8	6.9
600	2.0	38.2	6.4
700	2.1	38.4	6.6
800	4.1	40.0	8.0
1000	7.0	41.6	10.4

Volatile Constituents

Carbon black is by no means pure carbon, as was shown some time ago by Neal and Perrott (10). Various volatile constituents were found to exist in amounts as high as 10% or more of the total weight of the carbon black. More recently, attempts have been made to relate the amount of volatile matter with the rubber reinforcing characteristics of the carbon. Johnson (8) showed that a black with very high volatile content exhibited unsatisfactory behavior in rubber, the reinforcement being low and the cure retarded. In a later publication (9) the same author emphasized the effect of high oxygen content. Neal and Perrott had shown that much of the volatile matter consisted of oxygen, which was removable as carbon monoxide upon heating to high temperatures. Johnson concluded that high volatile content is accompanied by high accelerator sorption. Wiegand and Snyder (19), on the other hand, found the volatile test difficult to employ and unreliable as an indication of vulcanization characteristics.

The samples produced from pyrolysis waste gases under various conditions of channel heights and draft control have been examined. Samples were placed in a platinum crucible and heated to 105° C. to remove water. A tightly fitting lid was placed on the crucible, and the latter after being weighed was placed in an electric furnace at 950° C. for a period of seven minutes, then cooled in a desiccator and weighed.

Discussion of Volatile Determination

Table XIV shows the effect of channel height on the volatile content. Values are highest at small channel settings, falling off to a minimum as channel height is increased. At the greatest channel height there is definite indication of a small increase in volatile content. These results would be predicted because very low channel settings are likely to interfere with the flame in such a way as to favor incomplete combustion, with a consequent increased formation of tars, etc. The slight increase at high channel settings

TABLE XIV

EFFECT OF CHANNEL HEIGHT ON VOLATILE CONTENT

Sample	Channel height, in.	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation, kg. per sq. cm.	T_B kg. per sq. cm.	Volatile, %
C29	1.92	3.3	247	296	6.8
C17	2.44	4.4	253	302	5.8
C18	2.84	3.9	244	304	4.6
C19	3.20	3.4	228	285	3.7
C21	3.61	2.2	204	228	5.0

is likely to be caused by the reduction in channel temperature which takes place under these conditions. Further evidence for this conclusion may be found in the results of Drogin (4), who shows that the volatile content of the carbon recovered from the sides of the channel is much greater than that of the carbon removed from the face. The temperature of the sides of the channel is, of course, much lower than that of the face, which is directly in contact with the flames.

Values, obtained from the rubber tests, have been inserted in Table XIV. Some indication of possible correlation exists, in that the lowest volatile content is obtained when the rubber reinforcement is at a maximum. On the other hand, the greatest volatile content appeared at lowest channel settings, but the corresponding rubber reinforcement was not far from the optimum, and the corresponding sorption was very low.

The highly retarded cure and high sorption shown by samples produced at great channel heights are not reflected in the volatile test. It is clear, in the case of carbon black produced in this experimental plant, that the volatile test itself gives little indication of the vulcanization behavior to be expected of the sample.

Restriction of draft has already been shown to exert but a small effect on the tests that have been applied. As shown in Table XV the volatile content exhibits no correlation with this variable.

TABLE XV

EFFECT OF DRAFT CONTROL ON VOLATILE CONTENT

Sample	Draft, %	Yield, lb. per 1000 cu. ft.	Modulus at 500% elongation, kg. per sq. cm.	T_B, kg. per sq. cm.	Volatile, %
C22	100	3.1	235	290	4.0
C23	50	3.2	224	291	5.3
C24	38	3.5	249	311	4.2
C18	27	3.9	244	328	4.6
C25	21	3.5	249	321	6.0

The time during which the sample remains in the channel has a definite effect on the volatile content as would be expected, since the temperature of the channel is of the order of 400° C., which is sufficiently high to destroy most organic compounds, although some of the constituents of the tars probably consist of highly condensed ring systems which are known to be capable of resisting these temperatures. The volatile matter also includes oxygen that is probably present in a chemically combined state. Neal and Perrott found that continued heating at 445° C. removed considerable amounts of carbon monoxide. From both of these points of view longer heating at 400° C. caused by slow channel speed must therefore reduce the volatile content. Drogin (5), however, mentions that a larger number of burner tips producing higher temperatures in the burner house increases the volatile content. In the present case a reduction is noted, but no relation between this change and rubber reinforcement has appeared, as is shown in Table XVI.

TABLE XVI

EFFECT OF CHANNEL SPEED ON VOLATILE CONTENT

Sample	Time of reversal, sec.	Modulus at 500% elongation, kg. per sq. cm.	T_B, kg. per sq. cm.	Volatile, %
C26	2.4	243	302	4.6
C18	3.9	244	328	4.6
C27	7.6	245	316	3.0

It should be pointed out, however, that none of the samples that were produced in this laboratory exhibited a volatile content as high as that reported by Johnson in the case of certain blacks which behaved badly in rubber. Hence, the tests may be of use in identifying samples with particularly unfavorable properties.

Apparent Density

The apparent density was determined by tapping a known weight of carbon in a graduated cylinder until no further change in volume could be produced. The test is a relative one and may be applied only if the carbons have received identical mechanical treatment, as in the present case.

TABLE XVII

EFFECT OF CHANNEL HEIGHT ON APPARENT DENSITY

Sample	Channel height, in.	Apparent density
C29	1.92	0.079
C17	2.44	0.102
C18	2.84	0.105
C19	3.20	0.109
C21	3.61	0.131

A definite relation between channel height and apparent density has been found in the case of carbon black produced from pyrolysis off-gas. As is shown in Table XVII, the density increases in a regular manner with increase of channel height. This relation is similar to that found with dye sorption, and, therefore, bears the same relation to the rubber test.

Since the true density of all carbon blacks is probably the same, the apparent density may be taken as a measure of the distribution of particle size and of particle shape. It is, therefore, probable that the great channel height produces a larger proportion of fine particles which pack among the larger particles, thus giving a higher apparent density and increased sorption.

Apparent density determinations obtained with black from propane-butane did not produce such regular results, and while the general order was the same, various inversions appeared at intermediate channel heights. Draft control had no effect on the apparent density, while continued heating on the channel produced a sample of high density (0.14).

Conclusions

Channel height is undoubtedly the most important single variable affecting the properties of carbon black produced in an experimental plant under constant flame conditions (*i.e.*, burner tip and gas pressure). Proper adjustment of this variable is essential if the maximum yield of good quality carbon is desired, since rather sharp maxima exist in both yield and quality. The greatest yield is obtainable at channel settings approximately intermediate between the lowest channel height tolerated by the flame and the highest at which any recovery of carbon is possible. The rubber reinforcing properties of the carbon follow the yield, and at all events in the plant under discussion, the most valuable method of gauging quality would be to estimate the yield.

Restriction of the draft increases the yield only if it assists in the production of steadier flames, and when carried to the point of reducing luminosity it reduces the yield. Again the reinforcement of rubber follows the yield insofar as the latter is affected by the draft.

Channel height is one of the most important factors influencing the sorptive power of the carbon. The amount of sorption of methylene blue rapidly increases with channel height, so that the relation between channel height and the logarithm of sorption index is approximately a straight line. This means that in the region of channel heights between the lowest and the one giving maximum yield, both the sorption and rubber reinforcement are increasing. At channel heights above that of maximum yield, however, the situation is reversed, since reinforcement falls off as sorption increases. No general relation may, therefore, exist between sorption and reinforcement.

A consideration of the time of cure required to produce optimum tensile strength indicates that very high channel heights produce very retarded cures, while all other samples cured at almost the same rate. It may be said, with safety, that if the sorption is very great the cure will be retarded.

If the results obtained in an experimental plant may be considered to have general application, it is clear why the sorption test has given such indefinite results in the hands of previous investigators. The reinforcement of rubber is a complex phenomenon in which a number of factors play individual parts. Thus it is possible for two samples of carbon black to differ widely in sorptive power and yet show similar rubber reinforcement.

The volatile content of carbon black changes with channel height in a manner similar to the yield. This test, however, gives even poorer correlation with the rubber properties of the carbon, since the samples produced at high channel heights, and behaving very differently in rubber, contained very little more volatile than the optimum amount.

It is significant that carbon blacks produced from gas mixtures of widely different composition show very similar properties, the important factor in every case (with the same burner tip) being the position of the depositing surface in the flame.

In a small experimental plant it has been possible to vary the yield, sorption, and rubber reinforcing properties of the product. It is well to consider, however, just how closely these results may be related to those that would be obtained in full-scale practice. While the burners and channels were similar to those generally employed, the number and arrangement of the flames were so different that the temperature in the burner house was much lower and, hence, the atmospheric conditions were very dissimilar. It is nevertheless very significant that carbon blacks that exhibit properties so similar to those obtained in commercial plants should have been produced. No drastic differences in the fundamental process of carbon deposition may, therefore, have existed.

Since channel height is the all-important variable, it may be suggested that changes in the quality of carbon black coming from a given plant are due to variations in the effective channel height brought about by atmospheric disturbances and fluctuations in gas pressure. While the sorptive capacity is of little use to the rubber chemist as a test of the quality of an unknown sample, it bears a direct relation to the channel height at which the sample was produced. If determinations could be made rapidly enough, it should be possible to control the conditions in the apparatus by following the sorptive capacity of the carbon being produced at any given time.

Acknowledgment

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A STUDY OF CUPRENE FORMATION[1]

By J. M. Calhoun[2]

Abstract

The copper oxide catalyzed polymerization of acetylene to cuprene has been studied between 230° and 330° C. by the flow method. The reaction shows an initial induction period at the lower temperatures followed by a rapid rise to a maximum rate and a more gradual decrease. With increase in temperature the induction period becomes shorter, and the maximum rate attained becomes greater. If commenced at 330° C. the reaction is explosive. Analysis of the exit gas shows considerable ethylene and some free hydrogen, the amounts increasing with the temperature of the reaction. This indicates that the hydrogen split off in cuprene formation does not bear a constant ratio to the amount of cuprene formed. The yield of cuprene based on acetylene reacting is about 85% of theory, which is 4 to 10% lower than values based on a volume contraction of acetylene alone.

An exponential equation has been derived which expresses the rate of absorption of acetylene at 290° C. over a period of 72 hr. under the conditions of the experiment. The equation is integrated to give the quantity of acetylene absorbed at any time. This makes a prediction of yields possible. The heat of polymerization was calculated from the determined heat of combustion of cuprene. Various theories regarding the mechanism of formation and structure of cuprene are discussed, and the photochemical evidence of a chain reaction is supported.

Introduction

Cuprene is a substance about which very little is known. It is a light-brown, amorphous, solid, polymerization or condensation product of acetylene that can be prepared in a variety of ways, the most common of which depends on the catalytic action of copper or copper oxide. It was first reported in 1898 by Erdmann and Kothner (6) who passed acetylene over spongy copper at 250° C. They believed cuprene to be a complex copper acetylide, and proposed the formula $C_{44}H_{64}Cu_3$. At temperatures above 400° C. decomposition of the acetylene took place with deposition of carbon black. Alexander (1) a year later claimed that most of the copper could be removed from the cuprene by boiling with dilute acids, and he concluded that it was taken up only mechanically by the cuprene.

In 1900, Gooch and Baldwin (8) obtained cuprene at 225° C. using a cupric oxide catalyst, and from an analysis of the product suggested that cuprene was a mixture of hydrocarbons from $C_{12}H_{10}$ to $C_{16}H_{10}$. Sabatier and Senderens (25, p. 329 et seq.; 26) used reduced copper at 180° C. and obtained a formula $(C_7H_6)_n$. The formation of cuprene was accompanied by liquid and gaseous by-products consisting of olefinic and aromatic hydrocarbons. Kaufmann and Schneider (14) in 1922 made a series of combustion analyses of cuprenes obtained with both copper and copper oxide at temperatures of 230° to 250° C. These analyses gave empirical formulas of $C_{11}H_{10}$ to $C_{16}H_{10}$.

In view of recent evidence regarding the formation and nature of cuprene, none of these formulas can be considered as satisfactory. The only agreement is in the fact that some hydrogen appears to be split off during the polymerization.

The polymerization of acetylene to cuprene has been accomplished by a number of other methods. This indicates that copper is by no means essential to the reaction. Nickel and cobalt at 180° C. cause a very slow formation of cuprene, the major products being liquid and gaseous hydrocarbons (9, p. 172; 25). Increase in temperature causes decomposition and charring. Cuprene is also produced from acetylene by the action of the silent electric discharge (12, 13), a high frequency electro-magnetic field (23), high voltage cathode rays (4, 15, 21), ultra-violet light of a wave-length below 2537 Å (3, 11, 15, 16, 17, 18), mercury photo-sensitization (2, 22), and α-particles from radon (15, 24). Although the cuprenes obtained in many of these cases were present in quantities too small to analyze, the physical appearance and properties of the polymers were the same.

Cuprene is extremely inert. There is no known solvent for it, and it undergoes no chemical reactions except those of such severity that decomposition of the original substance is probable, *e.g.*, it is attacked by strong nitric or sulphuric acid and bromine at 130° C. under pressure (14). Cuprene cannot be sublimed *in vacuo* at 300° C., and at higher temperatures decomposition takes place. It burns slowly in air with a smoky flame. Physically, cuprene varies greatly with the conditions of preparation, and may be loose, soft and flocculent, or hard and comparatively dense. A number of uses for cuprene suggested in the literature are: a cork substitute, an ingredient in plastics, acid resistant and electrical insulation material, an absorbent for liquid explosives, a substitute for charcoal in black powder, etc. (10).

This investigation was undertaken because of the contradictory evidence in the literature concerning cuprene, and the general lack of information regarding the nature of the reaction. It was restricted to a study of the copper catalyzed polymerization by the flow method, the reaction being followed by measuring the rate of disappearance of acetylene at constant pressure under various controlled conditions.

Apparatus

The polymerization was carried out in a reaction chamber consisting of a Pyrex tube 1.25 in. in diameter and 24 in. long. An inlet and an outlet tube and a 360 degree Centigrade thermometer were fastened in the ends with rubber stoppers. A concentric iron pipe wound with nichrome wire and insulated with asbestos served as the heating unit. The 110 volt a-c. with three variable resistances in series was used for temperature control.

In preliminary experiments wet meters were used to measure the input and output of acetylene. However, even after careful calibration against a standard volume, they were found insufficiently accurate for the low rates of flow necessary. Two devices were then constructed to measure the volume of gas passed in and out of the reaction chamber.

Iron pipes 2 in. in diameter and 22 in. long were welded at both ends and fitted with ¼ in. pipe for the necessary connections. Two glass gauges were attached to each tank. The first gauge was a 50 cc. burette, which was connected to the tank at both top and bottom. The second gauge was connected to the tank at the bottom only, the top being left open to the atmosphere. Mercury reservoirs constructed of sheet iron were connected at the bottom to each tank by pressure tubing. A T-tube fitted with needle valves at the top of each reservoir provided an inlet and escape for compressed air. Each tank was connected to the system at the top through a three-way stopcock.

By applying air pressure to the reservoir, the mercury could be raised in the tank and in the glass gauges. When the level in both gauges was the same, the pressure in the tank was atmospheric. Each tank was calibrated with water so that the volume could be read from the graduated gauge. The tanks had a capacity of about 1200 cc., and the volume could be measured to within 1 cc.

The complete set-up is shown in Fig. 1. The acetylene, although 99% pure, was first passed through a purification train consisting of sulphuric acid to remove traces of phosphine, active carbon to remove organic sulphur
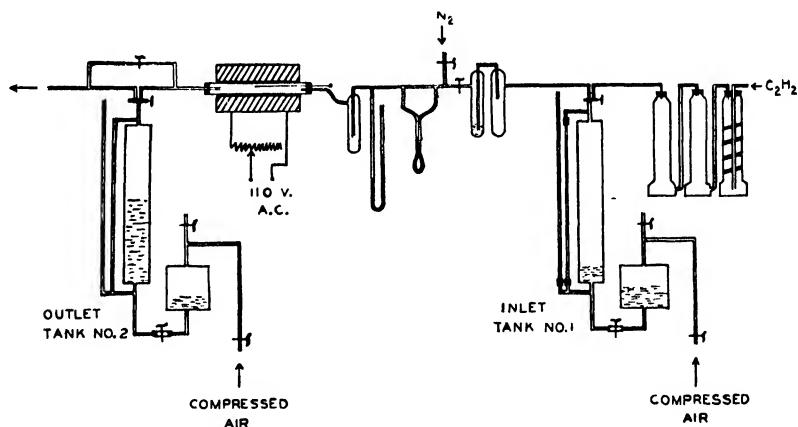
FIG. 1. *Apparatus.*

compounds, and soda lime for drying. After tank No. 1 was placed a bubbler, a flowmeter and a manometer, all containing oil and protected at each end by traps. A T-tube next to the flowmeter and a by-pass around tank No. 2 permitted flushing of the system with nitrogen.

At the beginning of a run, tank No. 1 was filled with acetylene and tank No. 2 with mercury. The catalyst, finely divided cupric oxide, was spread evenly on an aluminium foil carrier 15 by 5 cm. bent in a half cylinder and placed inside the reaction tube. The system was then completely flushed out with nitrogen. When the desired temperature was reached, the by-pass was closed and acetylene forced steadily from tank No. 1 to tank No. 2 under a slight positive pressure (about 1 cm. mercury). The rate of gas flow during

each run was made roughly double the rate of absorption in order that any by-products might be carried away from the reaction zone. The gas volume in both tanks was read at regular intervals, the pressure in the system being momentarily reduced to atmospheric. The apparatus was so designed that each tank could be filled or emptied independently of the system without interruption of the run. At the completion of the run the by-pass was opened, and the system again flushed with nitrogen. After cooling to room temperature the cuprene was removed and weighed.

Experimental Results

The Effect of Temperature on Cuprene Formation

A series of runs was made at different temperatures, using the same initial weight of catalyst but operating for different lengths of time. The cuprene formed as a spongy mass on the carrier, and, when removed, the catalyst was no longer visible. Small amounts of a greenish oil collected at the cooler end of the reaction tube. This oil was no doubt a mixture of aromatic and olefinic hydrocarbons as reported by Schläpfer and Stadler (27).

Table I shows the extremely rapid increase in the rate of cuprene formation with increase in temperature. The average yield of cuprene per hour per gram of copper increases from 2.89 gm. at 230° C. to 89.3 gm. at 310° C.

TABLE I

THE EFFECT OF TEMPERATURE ON THE YIELD OF CUPRENE

Run No.	11	7	8	16	15
Temp., °C.	230	250	270	280	310
Time, hr.	8	7	6	5	2
Rate of input flow, litres per hr.	0.25	0.5	0.75	1.5	3.0
Volume C_2H_2 absorbed, N.T.P., litres	0.475	1.340	2.020	3.040	3.260
Yield of cuprene, gm.	0.462	1.397	2.116	3.253	3.573
Average yield of cuprene per hr., per gm. of copper	2.89	9.97	17.6	32.5	89.3
*Apparent yield of cuprene, % theory	80.3	88.5	89.4	91.6	93.8
Copper content calculated, %	4.33	1.43	0.94	0.61	0.56
Copper content by ignition, %	3.60	1.17	0.69	0.80	0.52

*NOTE:—*The apparent yield of cuprene as per cent of the theoretical yield is calculated from the volume contraction of acetylene and from an empirical formula of $(C_2H_2)_n$ for cuprene. The errors involved in such a calculation are discussed after the section on gas analysis.*
    Weight of CuO used, 0.0250 gm.

The rate of cuprene formation is not uniform with time, so that the average yield per hour gives only a rough comparison, but is sufficient to show the important effect of temperature. At 230° C. the reaction is relatively very slow and the cuprene formed is rich in copper, and is loose and fluffy with almost no coherent qualities. It is brown, becoming lighter as the reaction proceeds and the copper content is reduced. Only at temperatures above 300° C. does the cuprene become darker.

The discrepancy between the calculated and analytical values for the copper content is due to the fact that some of the catalyst may remain on the carrier, while the balance is not necessarily evenly distributed throughout the cuprene.

The increase in the apparent yield of cuprene as per cent of the theoretical yield from 80.3% at 230° C. to 93.8% at 310° C. is quite striking. It can be due only to a difference in the proportion of oily by-products or tar formed to that of cuprene. Therefore the temperature coefficient for tar formation must be less than that for cuprene formation. In addition it may be observed (Table I) that the rate of gas flow was made greater at the higher temperatures to accommodate the more rapid formation of cuprene. That is, the time of contact of acetylene not polymerized to cuprene was less, and the quantity of by-products formed would be relatively smaller.

A clearer picture of what is happening is given by the rate of absorption of acetylene during each run (Table II). The times correspond to the mid-points in the time intervals over which the absorption was measured. This measurement does not distinguish between solid and liquid polymerization products, but since cuprene represents by far the largest portion, the rate of absorption of acetylene may be considered as a measure of the rate of cuprene formation.

TABLE II

THE EFFECT OF TEMPERATURE ON THE RATE OF ABSORPTION OF THE ACETYLENE

Run No.	11		7		8		16		15	
Temp., °C.	230		250		270		280		310	
	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption	Time	Rate of absorption
	1.0	0.5	0.25	1.6	0.25	18.0	0.125	27.6	0.167	111.6
	2.0	0.3	0.75	2.2	0.75	25.4	0.375	48.8	0.5	100.5
	3.0	0.2	1.25	13.4	1.25	25.8	1.0	42.1	0.833	92.4
	3.75	1.0	2.0	14.5	2.0	22.8	2.0	35.3	1.25	80.8
	4.25	0.9	3.0	12.9	3.0	19.1	3.0	30.5	1.75	72.6
	4.75	5.2	4.0	11.9	4.0	15.0	4.0	27.0		
	5.25	7.5	5.0	10.5	5.0	12.7	4.75	24.0		
	5.75	9.2	6.0	9.8	5.75	11.6				
	6.25	6.0	6.75	9.6						
	7.00	6.3								
	7.75	6.2								

NOTE:—*Time in hours; rate of absorption of acetylene in litres per hour per gram of copper, measured at 25° C., 760 mm.*

The data are plotted in Fig. 2, which illustrates several striking features. There is an initial induction period for the reaction, followed by a rapid rise to a maximum rate and a more gradual decrease. With increase in temperature the induction period becomes shorter and the maximum rate attained becomes greater. Above 280° C. the rate of absorption of acetylene is already
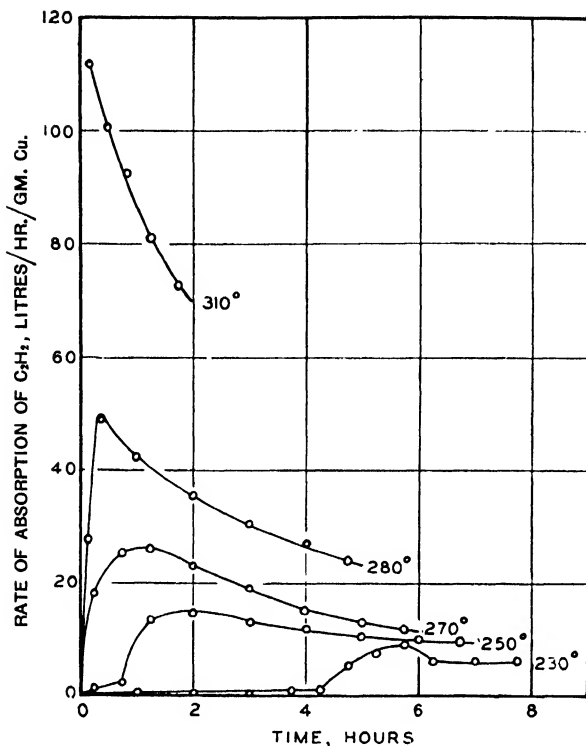
FIG. 2. *Effect of temperature on rate of absorption of acetylene.*

below the maximum before the first reading can be taken. An interpretation of this behavior will be left for a later section. It may be noted that the area beneath the rate curves corresponds to the quantity of cuprene formed, and explains the great effect of temperature on yield.

Two attempts to operate at 330° C. resulted in small explosions with an immediate deposit of carbon black throughout the apparatus. However, if a run was begun at 290° C. and the temperature raised gradually to 330° C., or even higher, no explosion occurred. The explanation for this can be found in Fig. 3, which shows the maximum rate of absorption attained (the peaks of the curves in Fig. 2) plotted against temperature.
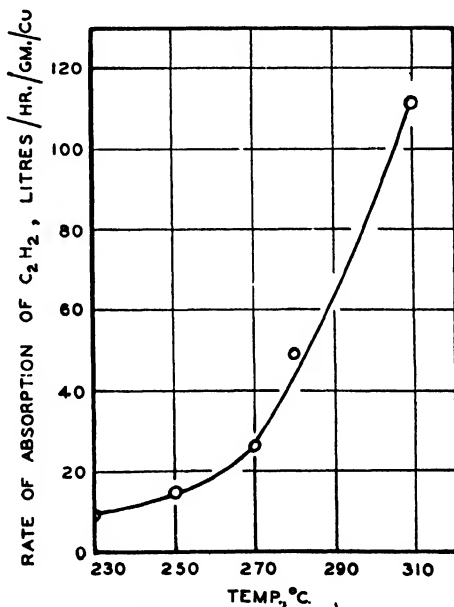
FIG. 3. *Maximum rate of absorption of acetylene.*

The maximum rate, which for practical purposes is the initial rate at high temperatures, increases very rapidly, and at 330° C. is so great that the exothermic nature of the reaction causes a sudden further elevation of temperature resulting in decomposition of the acetylene and deposition of carbon black. If, however, the reaction is initiated at 290° C. the rate is well below the maximum before 330° C. is reached, and no explosion occurs.

Analysis of the Exit Gas

An analysis of the exit gas in several runs was made, since the identification of gaseous by-products might throw some light on the nature of the reaction. If cuprene contains less hydrogen than acetylene as claimed in the literature, the hydrogen split off should be present in the by-products either free or combined with excess acetylene.

Three runs were made at different temperatures to collect samples of the exit gas. The quantities of catalyst and rates of gas flow were chosen to give large amounts of cuprene and a high concentration of impurities (if any) in the exit gas. At the close of each run, the reaction tube was flushed with acetylene to collect all the impurities in tank No. 2, from which two gas samples were taken. The gas was analyzed in duplicate in an Orsat apparatus. Since it was essential to distinguish quantitatively between acetylene and ethylene, ammonium cuprous chloride reagent was unsatisfactory. Absorption in fuming sulphuric acid gave the total unsaturates. Acetylene was then estimated on a separate sample by absorption in neutral silver nitrate solution and titration of the nitric acid liberated. Ethylene does not interfere, and was obtained by difference.

Table III gives the data for each run and Table IV the analysis of the exit gas. The amount of nitrogen is higher than that expected, although small amounts may be present in the acetylene and the ratio of input gas to exit gas is from four- to sevenfold. The apparatus was found to be free from air leaks which would be improbable with the system under a positive pressure.

TABLE III

PREPARATION OF CUPRENE FOR COLLECTION OF EXIT GAS

Run No.	27	25	26
Temp. ° C.	245–255	280–300	330–350*
Weight of CuO used, gm.	0.0531	0.0526	0.0464
Time, hr.	4.383	2.500	2.167
Rate of input flow, litres per hr.	1.0	2.5	2.9
Volume of gas input, litres	3.636	5.599	5.570
Volume of gas output, litres	0.906	0.815	0.956
Apparent contraction, litres	2.730	4.784	4.614
Yield of cuprene less copper, gm.	2.80	5.12	4.88
Apparent yield of cuprene, % theory	88.6	92.1	90.9

Reaction started at 290° C. to prevent explosion. Temperature raised to 330° C. in 20 min.
Note:—All gas volumes at N.T.P.

TABLE IV

ANALYSIS OF EXIT GAS

Run No.	27		25		26	
Temp. ° C.	245–255		280–300		330–350	
CO_2	0.8	0.8	0.5	0.1	0.4	0.1
O_2	0.8	0.6			1.2	0.7
C_2H_2	75.0	74.7	47.8	48.2	26.8	26.1
C_2H_4	12.5	12.8	35.1	34.8	46.0	47.0
C_2H_6	0.0	0.2	0.3	0.3	0.5	0.7
H_2	1.5	0.3	3.0	3.0	7.9	6.8
N_2	9.4	10.6	13.3	13.6	17.2	18.6

The most interesting feature is the large amount of ethylene produced, which together with some free hydrogen and traces of ethane all increase with the reaction temperature. It is believed that the hydrogen is split off from the cuprene after the acetylene is polymerized, and that such an elimination is not essential to the mechanism of the reaction. Ethylene and ethane are then formed by the catalytic hydrogenation of excess acetylene. The yields are calculated on this basis and given in Table V.

TABLE V

CALCULATION OF YIELDS

Run No.	27	25	26
Temp., °C.	245–255	280–300	330–350
Products recovered, litres:			
$\quad$ C_2H_2 polymerized to cuprene	2.412	4.410	4.204
$\quad$ C_2H_4	0.115	0.285	0.444
$\quad$ C_2H_6 ·	0.001	0.002	0.006
$\quad$ H_2	0.008	0.024	0.071
True contraction, litres	2.738	4.808	4.685
Total C_2H_2 reacted, litres	2.854	5.095	5.135
Yields,-% by volume of C_2H_2 reacted:			
$\quad$ C_2H_2 polymerized to cuprene	84.5	86.5	81.8
$\quad$ C_2H_4	4.03	5.60	8.65
$\quad$ C_2H_6	0.03	0.05	0.12
$\quad$ Tar (by difference)	11.4	7.8	9.4
$\quad$ Free H_2	0.28	0.48	1.38
Total H_2 split off:			
$\quad$ % by volume of C_2H_2 reacted	4.37	6.18	10.27
$\quad$ % by weight of C_2H_2 polymerized to cuprene	0.40	0.55	0.96

The quantity of each impurity was determined from the volume of exit gas and its average composition. Since free hydrogen represents an increase in volume, this amount was added to the apparent contraction to give the true

contraction of acetylene. Ethylene and ethane represent no volume change, but must be added to the true contraction to give the total acetylene reacted. The yields of each product are then calculated on this basis. The total hydrogen split off equals the free hydrogen, plus the ethylene, plus two times the ethane. This does not take into account the tar, which may be hydrogenated to a slightly greater or smaller degree than is acetylene.

If the elimination of hydrogen were an essential step in the polymerization, one would expect a constant proportion of carbon to hydrogen in cuprene, irrespective of the conditions of preparation. This is not the case. Combustion analyses of cuprenes prepared by Kaufmann and Schneider (14) at 230-240° C. gave percentages of hydrogen varying from 5.25 to 6.88. The theoretical amount in acetylene is 7.74%, and therefore a loss of 0.86 to 2.49% occurred. Table V shows that the elimination of hydrogen from the cuprene prepared by the writer amounted to only 0.40% at 245–255° and 0.96% at 330–350° C. Therefore such formulas as $(C_7H_6)_n$ and $(C_{15}H_{10})_n$ proposed for cuprene in the literature are not applicable.

Photochemical evidence, referred to later, shows that cuprene corresponding to $(C_2H_2)_n$ has been prepared, and that either no free hydrogen was found, or that it was observed only after the polymerization was completed (15, 19). It is, therefore, suggested that hydrogen is split off by slight thermal decomposition of the cuprene itself after polymerization, and not by an elimination essential to the mechanism of the reaction. Additional evidence for this is in the fact that the amount of hydrogen split off increases with the reaction temperature, and that cuprene is known to be thermally unstable even when heated in an inert atmosphere.

That the formation of hydrogen and ethylene could be due to the decomposition of acetylene, entirely independent of cuprene formation, is not impossible. This, however, would involve the deposition of carbon black which was not observed under the conditions of the experiment, either on the walls of the reaction chamber or upon examination of the cuprene under a microscope. It is believed that the evidence of combustion analyses reported in the literature, the instability of cuprene, and the fact that no carbon black could be found, favors the reactions as outlined. In any case it does not affect the conclusions drawn regarding the formation of cuprene itself, and the error involved in the calculation of theoretical yields would be small.

The difference between the apparent yield of cuprene determined by a volume contraction alone and the true yield as calculated above is considerable. All yields of cuprene reported in the literature and based on a volume contraction of acetylene are too high by as much as 4 to 10%. The apparent yields of cuprene are still, of course, comparable. Any error involved in the use of the empirical formula $(C_2H_2)_n$ for cuprene for the calculation of yields is negligible because of the small amount of hydrogen removed. The yield of tar, as shown in Table V, is greatest at the lowest temperature. This again is largely due to the decreased rate of gas flow and the longer time of contact of the acetylene. At 280° to 300° C. the yield of tar is least, and at 330° to

350° C. it is again somewhat greater, owing probably to the extreme of temperature, since the time of contact is roughly the same.

It is interesting to note that Fischer and Peters (7) prepared cuprene in a liquid medium and obtained yields similar to the above. Copper was deposited on kieselguhr and suspended in methyl naphthalene. The reaction was carried out in the presence of hydrogen at 230° C.; 86.1% of the acetylene was recovered as cuprene and 12.4% as ethylene. The excess of hydrogen would account for the larger proportion of ethylene.

An Equation for the Rate of Absorption of Acetylene in Cuprene Formation

It was observed that many of the rate curves for the absorption of acetylene in cuprene formation at the higher temperatures appeared to be of the exponential type. A run was therefore made over a long period of time to obtain as accurate data as possible for a mathematical analysis of the curve. If an equation could be established it would be very useful for the prediction of rates and yields, and might in addition prove of theoretical interest.

The data and calculations are given in Table VI. After 32 hr. running, the reaction was continued for another 40 hr. without supervision. During

TABLE VI

THE RATE OF ABSORPTION OF ACETYLENE DURING CUPRENE FORMATION

t	y (experimental)	y_1 $31.1e^{-0.0325t}$	y_2 $14.7e^{-0.222t}$	y_3 $45.4e^{-1.135t}$	$y_1+y_2+y_3 = y$ (calcd.)
0.05	105	31.0	14.6	42.8	88.4
0.15	91	30.9	14.2	38.2	83.3
0.3	81.5	30.8	13.8	32.2	76.8
0.5	70.0	30.6	13.2	25.8	69.6
0.8	61.5	30.3	12.3	18.3	60.9
1.25	50.8	29.8	11.1	11.0	51.9
1.75	47.2	29.4	10.0	6.2	45.6
2.5	39.2	28.7	8.5	2.7	39.9
3.5	34.2	27.8	6.7	0.8	35.3
4.5	32.3	26.9	5.4	0.3	32.6
5.5	31.0	26.0	4.3		30.3
7.0	28.3	24.8	3.1		27.9
9.0	24.9	23.2	2.0		25.2
11.0	23.3	21.8	1.3		23.1
13.0	22.1	20.4	0.8		21.2
15.0	18.9	19.1	0.5		19.6
17.0	17.7	17.9	0.3		18.2
19.0	16.8	16.8	0.2		17.0
20.5	16.0	16.0	0.1		16.1
23.0	14.2	14.7			14.7
25.0	13.3	13.7			13.7
27.0	12.9	12.9			12.9
29.0	13.0	12.1			12.1
31.0	11.0	11.4			11.4
49.0	4.7	6.3			6.3
72.5	3.2	3.0			3.0
100.0		1.2			1.2
200.0		0.05			0.05

Run No. 78; temp., 290° C.; weight of CuO *used, 0.0125 gm.; t = time, hr.; y = rate of absorption of acetylene, litres per hr. per gm. copper at 25° C., 760 mm.*

this time the temperature varied somewhat, but it was held constant at 290° C. for a period of one hour for each reading. This would not cause much error at the lower end of the curve, since we were interested in the rate of absorption, rather than in the quantity of acetylene absorbed. In Column 1, Table VI, the time in hours, t, corresponds to the midpoint of the interval over which the absorption was measured. Column 2 shows the experimentally determined rate of absorption of acetylene, y, measured in litres per hour per gram of copper at 25° C., 760 mm.

The equation for the rate curve was determined as follows. Fig. 4 shows a plot of (log y, t), the values of y being taken from the smoothed experimental rate curve. It is seen that for $t > 17$ a straight line is obtained, and the
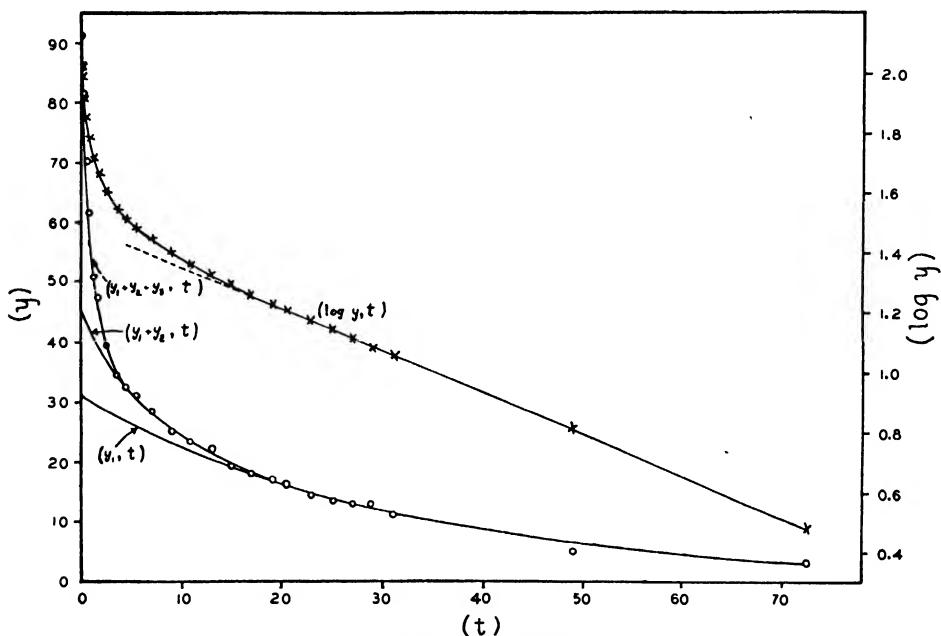
FIG. 4. *Rate of absorption of acetylene during cuprene formation at 290° (run No. 78).*
$y_1 = 31.1e^{-0.0325t}$; $y_2 = 14.7e^{-0.222t}$; $y_3 = 45.4e^{-1.135t}$.

equation of this portion of the curve is therefore of the type, $y = ae^{bt}$, where a and b are constants. The constants are evaluated by the method of averages. This gives the equation:

$$y_1 = 31.1e^{-0.0325t} \qquad (1)$$

Values of y are then calculated for $t < 17$, and the difference between the calculated and experimental values of y is plotted against t. An equation of this difference curve is obtained in a manner similar to that adopted before. This makes the equation valid for $t > 4.5$.

A second difference curve for $t < 4.5$ is obtained by repeating the process. This gives as the final equation for run No. 78:

$$y = 31.1e^{-0.0325t} + 14.7e^{-0.222t} + 45.4e^{-1.135t}, \qquad (2)$$

which is valid for all values of $t > 0.3$.

Table VI shows the calculated values for each term of the equation (Columns 3, 4, 5) which are summed in Column 6. A comparison of the calculated and experimental values for $t > 0.3$ shows good agreement. This is borne out in Fig. 4, which shows how close the experimental points come to the calculated curve. An extrapolation of the curve is of interest, although the validity of the equation is not certain much beyond the experimental values.

Equation (2) can be integrated to give the total quantity of acetylene absorbed, x (litres per gram of copper at 25° C., 760 mm.) at any time, t:—

$$x = 1066 - 957e^{-0.0325t} - 66.2e^{-0.222t} - 40.0e^{-1.135t} \qquad (3)$$

The constant of integration is found by substituting experimental values of x and t. A few experimental and calculated values are compared in Table VII, and it is seen that the agreement is very good. The average error for 38 values is only 0.5%.

The extrapolated values show very clearly how the reaction slows up. The equation would predict a limiting value of $x = 1066$ at infinite time, but this is not necessarily true. The volume of acetylene absorbed may be converted readily to grams of cuprene, if an apparent yield of, say 90%, is assumed. A calculation of the copper content of the cuprene at various stages based on this value is . given in the last column of Table VII. It is seen that 0.1% copper appears to be about the minimum obtainable under the conditions of the experiment.

TABLE VII

THE QUANTITY OF ACETYLENE ABSORBED DURING CUPRENE FORMATION.

t	x (exptl.)	x (calcd. from Equation (3))	Copper in cuprene, calcd., %
0.4	35.9	35.4	2.9
1.0	74.5	74	1.4
2.0	123.5	123	0.85
4.0	196.9	198	0.52
6.0	260.2	262	0.40
8.0	316.9	317	0.33
10.0	360.7	367	0.28
15.0	475.9	476	0.22
20.0	563.6	565	0.18
25.0	637.3	641	0.16
30.0	702.0	705	0.15
49.0		871	0.12
72.5		975	0.11
100		1029	0.10
200		1065	0.097
1000		1066	0.097

NOTE:—*Run No. 78; t = time, hr.; x = total volume of acetylene absorbed, litres per gm. of copper at 25° C., 760 mm.*

Any theoretical interpretation of the above equation at the present time would be difficult if not impossible, because of the complicated nature of the reaction. In addition to possible kinetic factors, the rate is influenced by mechanical factors such as the enclosure of the catalyst within the cuprene, decrease in surface as the cuprene builds up in the cylindrical tube, and diffusion of the acetylene through the cuprene. A further complication is caused by side reactions and tar formation.

The chief value of such an equation would be to predict rates and yields. The constants of course will vary with the experimental conditions, but the

available data indicate that an exponential equation is generally applicable, the number of terms depending on the range and accuracy desired. At temperatures at which the induction period becomes appreciable, this would have to be taken into account in the equation.

The Heat of Combustion of Cuprene

The heat of combustion of several samples of cuprene was obtained through the courtesy of Dr. O. J. Walker, University of Alberta. The results are given in Table VIII. Since the heat of combustion of acetylene is approximately 312 kcal. per mole, the heat of polymerization may be calculated and is found to be 61 to 70 kcal. per mole of acetylene polymerized. This shows the strongly exothermic nature of the reaction.

TABLE VIII
THE HEAT OF COMBUSTION OF CUPRENE

	Run No.		
	19	21	78
Temp., °C.	290	290	290
Time, hr.	5	5	72
Copper content, calcd., %	0.50	0.47	0.09
Heat of combustion, cal./gm.	9396 9224 9307	9320 9311	9635 9673
Average	9309	9315	9654

In a paper published since this work was completed, Lind (19) states that α-ray cuprene undergoes spontaneous oxidation in air at room temperature which is nearly complete in 12 or 15 days. He found the heat of combustion of unoxidized cuprene to be 10,203.7 cal. per gm. and that of oxidized cuprene, 7,113.5 cal. per gm. compared with the above values of 9300 to 9600. Lind also calculated for unoxidized cuprene a heat of polymerization of 47 kcal. per mole of acetylene. The calorimetric determinations reported in Table VIII were made six months after the preparation of the cuprene, when any oxidation would presumably be complete. This might account for the discrepancy in the values for the heat of combustion and the rather high heat of polymerization.

Discussion

The polymerization of acetylene to cuprene is of such a complex nature that it is difficult to theorize regarding the mechanism of formation and structure of the polymer. However, various theories proposed in the literature will be discussed in the light of the evidence obtained here, and a possible explanation offered.

Cuprene is chemically almost inert, and there is no known solvent for it. It does not swell as do rubber and cellulose in suitable agents, and it cannot be sublimed *in vacuo*. In fact, all the properties of cuprene indicate a substance of such complexity that no simple formula can be entertained. Its molecular weight must be extremely high, or rather it is in the range where molecular weights become meaningless.

Sabatier and Senderens (26) first suggested that copper formed an unstable acetylide capable of reacting with additional acetylene to give a condensed molecule:

$$n \ C_2H_2 \ + \ n \ Cu \ \longrightarrow \ n \ C_2Cu \ + \ n \ H_2$$
$$n \ C_2Cu \ + \ 6n \ C_2H_2 \longrightarrow \ (C_7H_6)_{2n} \ + \ n \ Cu$$
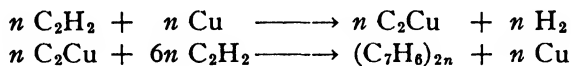
The equations are based on his formula for cuprene, which cannot be considered valid because of the varying proportions of hydrogen to carbon found. Sabatier claims that the regenerated copper reacts indefinitely, while the hydrogen set free combines with unused acetylene to give ethylene.

The photochemical polymerization of acetylene yields more information regarding this reaction. Under the action of α-particles or cathode rays, ionization first takes place, and Lind (15) claims that 20 molecules of acetylene are polymerized for every pair of ions produced. Lind was unable to find a solvent for the polymer, and X-ray examination gave no clue to its structure. He also observed that free hydrogen was produced *after* most of the acetylene was polymerized, owing to bombardment of the cuprene by α-particles. The total amount of hydrogen liberated was only 2% of the acetylene polymerized. This indicated that the formula $(C_7H_6)_n$ of Sabatier and Senderens could not apply. However the molecular weight of cuprene must be many times greater than $(C_2H_2)_{20}$. In a later paper Lind (20) states that no hydrogen is produced by an electric discharge on a wall skin of cuprene in many hours.

Bates and Taylor (2) in 1927 studied the polymerization of acetylene by ultra-violet light, and proposed a mechanism based on an activation of acetylene molecules by the absorption of a quantum of energy:

$$C_2H_2 \ + \ h\nu \ \longrightarrow \ C_2H_2*$$
$$C_2H_2* + \ (n \ - \ 1)C_2H_2 \ \longrightarrow \ (C_2H_2)_n$$
$$\text{(cuprene)}$$
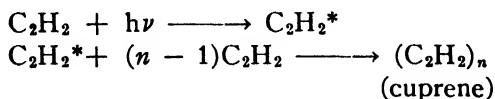
The activated acetylene molecules then add on additional acetylene by a chain mechanism.

Melville (22), studying the mercury photosensitized polymerization of acetylene, found no secondary reactions such as the elimination of hydrogen. He concluded that an excited mercury atom on collision with an acetylene molecule formed a complex of the acetylide type, then adding on additional acetylene by a chain mechanism. His calculations indicated a chain length of 10 at 20° and 100 at 250° C., but since the polymer was not volatile at 300° *in vacuo*, he concluded that a secondary polymerization of the products of the gaseous chain reaction took place.

Dostal and Mark (5) have shown that the polymerization of many unsaturated substances is a chain reaction. It is believed that some such mechanism is the most probable explanation for the formation of cuprene. Stepwise addition of acetylene molecules with a shift of hydrogen atoms would be too slow and would yield only low polymers. The fact that no low polymers are found, and that cuprene is formed in the first few seconds of reaction, is strong evidence for a chain mechanism. The following outline conforms to the findings of a recent symposium on polymerization and condensation.*

The initiation of chains is brought about by the collision of two acetylene molecules to form a nucleus. This requires activation by photochemical, thermal or catalytic means which may occur mono- or bimolecularly. In the case of the catalyzed reaction, the copper probably forms an intermediate compound of the acetylide type, and is later eliminated. Evidence for this is found in the fact that the copper becomes distributed throughout the cuprene. The nucleus then reacts with additional acetylene molecules, and this results in growth of the polymer. The energy of activation of this reaction is usually lower than that required for the initiation of chains, so that chain growth can be more rapid than the formation of nuclei. This explains the preliminary induction period observed at lower temperatures, and is characteristic of chain reactions. Increase in temperature shortens the induction period, until, at 330° C., the reaction becomes explosive, another characteristic of chain reactions.

The rate of polymerization by a chain reaction depends on the relative rates of initiation, propagation and termination of chains. As the length of the chains increases, the number of active points at which another acetylene molecule can add becomes smaller. The exponential decrease in rate of cuprene formation observed may be due to this increasing steric factor as the chains become longer, plus such mechanical effects as have already been discussed. However, since cuprene is not deposited throughout the reaction chamber, but grows only on the catalyst carrier, the reaction is not homogeneous but probably occurs in the solid phase. Acetylene molecules will then have to diffuse farther into the cuprene as reaction continues, and the over-all rate may be governed by a diffusion process.

Termination of the chains may be brought about by collisions with the growing polymer of a kind different from that responsible for propagation. If the nuclei still contain double bonds, these may be reduced by thermal or catalytic means, and the valencies set free are used for linking chains together to give a two or three dimensional lattice. The product so obtained has properties quite different from those of ordinary chain polymers, especially in regard to solubility, melting point, and elasticity. That such a secondary polymerization or condensation occurs is shown by the fact that a linear chain of even 5000 chain atoms will swell strongly in suitable solvents and form highly viscous solutions. No such solvent has ever been found for cuprene, and only cross-linkages and a lattice structure can account for its behavior.

* *"The phenomena of polymerization and condensation".* (*A general discussion held by the Faraday Society*). *Gurney and Jackson, London. 1935.*

The above explanation accounts equally well for the formation of cuprene by all the diverse methods. Small amounts of hydrogen are undoubtedly split off, but this is believed to be due to thermal decomposition after polymerization and not to an elimination fundamental to the mechanism of the reaction, as was previously mentioned. In the case of cuprene prepared by some methods, free hydrogen is either entirely lacking or is observed after the acetylene is polymerized. When hydrogen is split off, it combines with excess acetylene to form ethylene. Thus the most recent evidence favors a basic empirical formula for cuprene of $(C_2H_2)_n$ and a structure of extreme complexity.

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THE HEAT CONTENT OF WATER SORBED ON CELLULOSE[1]

By J. H. Shipley[2], W. Boyd Campbell[3] and O. Maass[4]

Abstract

The specific heat of cellulose has been determined for the temperature range −70° to 25° C. The heat capacity of water sorbed to the extent of 5.92 and 12.0% by cellulose has been determined for the range −78.5° to 25° C. These data are compared with the heat capacity of pure water for the same range of temperature, viz., −78.5° to 25° C.

Introduction

The system cellulose-water has been intensively studied in this laboratory. Adsorption and desorption isothermals, the dielectric constants of adsorbed water vapor, the density of adsorbed water, and the heats of wetting at various stages of water adsorption are being studied (1, 2, 5, 6). The objective of this work is to establish a better understanding of the mechanism of water adsorption and of the physical structure of cellulose.

The present paper is a preliminary one on the measurement of the specific heat of cellulose and of the specific heats of water adsorbed to the extent of 6 and 12%. These measurements were made for the range −78° to 25° C., since a comparison can be made with the heat content of free water for this range as determined by Barnes and Maass (4).

Apparatus

An adiabatic, radiation-thermocouple calorimeter as described by Barnes and Maass (3) was employed. Owing to the difficulty in compacting cellulose, with the consequent relatively small volume-heat capacity as compared to that of free water, a small inner calorimeter containing 175 gm. of water was used. The thermal-galvanometer system was arranged to give a sensitivity of 0.0002° C., and the outer bath could be controlled to within 0.001° C. of the temperature of the calorimeter for definite periods. The monel metal container for the cellulose was that used by Hampton and Mennie (8) in their investigation on gelatine.

Procedure

The cellulose was purified from absorbent cotton by treatment with sodium hydroxide and acetic acid in the manner described in detail by Argue and Maass (1).

This "standard" cellulose was introduced into the clean, weighed, monel metal container, which was then placed in an electric oven for 10 hr., the temperature being maintained at 100° C. Meanwhile, air, dried over concentrated sulphuric acid and phosphorus pentoxide, was passed through the cellulose by means of a hypodermic needle reaching to the bottom of the container. While still in the oven the cover was attached, and, after cooling, the container plus the dry cellulose was weighed. It was found that this weight could be duplicated after the cellulose readsorbed water and then was dried again under the above conditions. This showed that the cellulose was rendered bone-dry by such treatment.

The filled container was prepared for immersion in the calorimeter by suspending it from a cork by a thread of the proper length and placing it in a closely fitting copper tube. Two discs, one of cardboard and the other of copper, were placed above the container inside the copper tube to prevent convection currents, and a piece of adsorbent cotton was placed just below the cork to prevent moisture from creeping into the tube and condensing on the container. Adhesive tape was wrapped tightly around the cork and the top of the tube to prevent the entrance of moisture.

The tube with the container was placed in the requisite cooling bath to bring the container to the required initial temperature. For a temperature of −78.5° C. solid carbon dioxide moistened with acetone was used, while for −38.5° C. and −6.25° C. a bath of ether, stirred by means of a current of air, was used. The bath was maintained at the proper temperature to within ±0.1° C. by dropping, from time to time, small pieces of solid carbon dioxide into the ether bath.

In the meantime the calorimeter was assembled as described by Barnes and Maass (3). About 175 gm. of water was introduced into the inner vessel from a weight pipette. The two baths were then brought to thermal equilibrium at the proper temperature, and the temperature was read every five minutes, the deflection of the galvanometer being kept at zero. This was done for 15 to 20 min. to determine the initial temperature of the calorimeter.

The container was then quickly lifted out of the copper tube and lowered into the calorimeter. The transfer took about two to three seconds, and the time at which it was effected was noted exactly. The fall in temperature was followed by running ice cold water into the outer bath, and keeping the two baths in thermal equilibrium as closely as possible. The temperature was recorded until a uniform change took place. This indicated the final temperature.

Water was introduced into the cellulose to the required percentage by means of steam and was accurately determined by weighing the container before and after adsorption.

Although the adsorbed water contributes only from 3 to 7% of the total heat effect, the error introduced was not as large as would at first be apparent. The largest error was a systematic one, and was due to heat gained by the

container when it was transferred from the initial cold bath to the calorimeter. Since this transfer was effected in the same manner and time and under approximately identical conditions for all the experiments, the error so introduced would tend to cancel out when the values for the total heat gained by the container plus cellulose are subtracted from the values for the container plus cellulose plus water to give the heat content of the sorbed water.

In all cases the heat capacities were corrected to a final temperature of 25.00° C.

Results

In Table I are given the total heats of the container and contents between the initial temperatures given in Column 1 and the final temperature. Each one is the mean of at least three determinations. In the case of the empty con-

TABLE I

TOTAL HEATS (CALORIES) GIVEN UP BY CALORIMETER CORRECTED TO FINAL TEMPERATURE, 25.00° C.

Initial temp., °C.	"Standard" cellulose	5.92% water	12.0% water	Empty container
−78.5	695.1	716.8	745.3	601.7
−38.5	439.9	452.0	472.9	371.0*
−25.0				298.7
− 6.25	222.3	229.9	238.3	183.2*

*Calculated values.

tainer, determinations were made from only two initial temperatures as the heat content varied continuously with the temperature. The container was made up of 59.121 gm. of monel metal and 3.068 gm. of lead. Allowing for the specific heat of lead, the specific heat of monel metal agrees with the values obtained by Horn (9) when these are extrapolated to the lower temperatures. Since the major error involved is due to heat gained by the container during transfer, this would appear in the specific heat of the container and not in that of the cellulose.

The heat content (Table II) of the "standard" cellulose is obtained by subtracting the heat content of the container from that of the container plus cellulose. The heat contents of the "5.92%" water and the "12.0%" water, per gram of water, given in Table II, were obtained by subtracting the values

TABLE II

TOTAL HEATS (CALORIES) PER GRAM OF MATERIAL CORRECTED TO FINAL TEMPERATURE, 25.00° C.

Initial temp., °C.	"Standard" cellulose	5.92% water	12.0% water	Free water
−78.5	23.5	92.0	105.0	138.2
−38.5	17.3	51.6	69.0	122.5
− 6.25	9.8	32.3	33.6	107.5

given in Column 2 from Columns 3 and 4 (Table I) respectively, and then recalculating on the basis of one gram of water. The last column in Table II gives the total heats of one gram of free water as determined by Barnes and Maass (4).

In Fig. 1 the heat contents of one gram of "standard" cellulose are represented graphically. By plotting this curve on a large scale and taking tangents, the specific heats of cellulose were calculated, and are given in
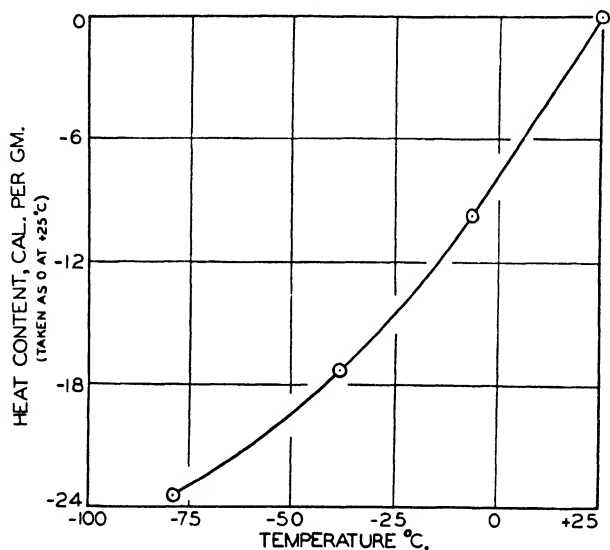
FIG. 1. *Heat content of cellulose from* $+25°$ *C.*

Table III. The only values for the specific heat of cellulose that have been published are those of Padoa (10), who gives a value of 0.347 between 0° and 80° C., and of Fleury (7), who gives a value of 0.366 at room temperature. As a matter of interest the specific heats of dextrin and dextrose are also given in Table III. Dextrin has the same empirical composition as cellulose, while dextrose has one more molecule of water. The authors intend to redetermine the specific heats of these and other carbohydrate compounds for the same temperature range used for cellulose, as apparently some interesting conclusions might be drawn.

TABLE III

SPECIFIC HEATS

Temp., °C.	Cellulose	Dextrin	Dextrose
−60	0.152		0.206
−40	0.187		0.230
−20	0.234		0.253
0	0.290	0.292	0.277
20	0.346	0.311	0.300

In Fig. 2 the heat content of free water is depicted in comparison with the heat contents of the "5.92%" water (Curve III) and "12.0%" water (Curve II). Curve I was obtained by subtracting Column 3 from Column 4, Table I, and recalculating on the basis of one gram of water. It, therefore,

represents what might be called the "12.0%" minus "5.92%" water. It is obvious that the latent heat of fusion is absent in the "5.92%" water, and the question arises whether this is due to supercooling or whether this water is not free water but in the nature of surface-combined water.
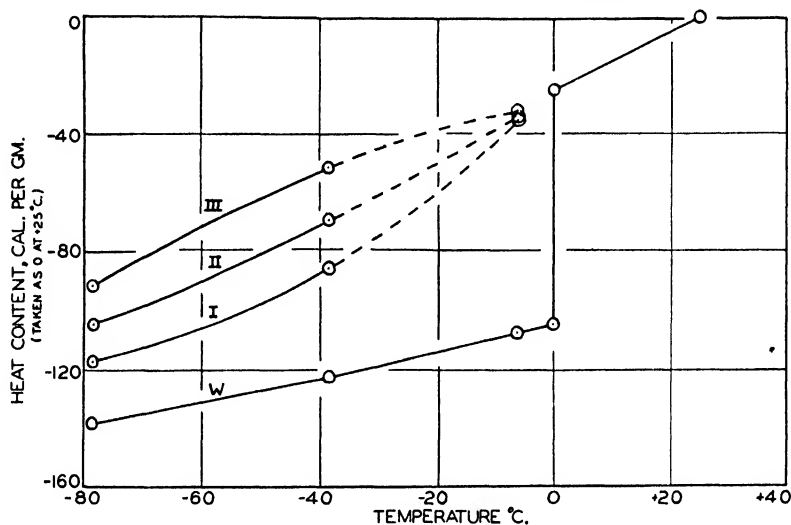
FIG. 2. *Heat content of water from* +25° C. *W, free water; I, "12% minus 5.92%" water; II, "12%" water; III, "5.92%" water.*

Curve II appears to be continuous with the heat content curve of free water in the liquid state and would therefore point to the existence of supercooled water. Curve III indicates that this is fortuitous and that the problem is not quite so simple. The two taken together may indicate that some small part of the adsorbed water has a heat capacity that is lower than that of free water, and that the remainder exists in some other form partly in the solid state, the enhanced values in this region being due to a latent heat of fusion. Curve I indicates that something of the kind has taken place.

Further experiments will be necessary to determine what takes place in this region. For this purpose a more refined technique is being developed so that smaller amounts of adsorbed water can be examined with accuracy.

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STUDIES ON HOMOGENEOUS FIRST ORDER
GAS REACTIONS

VI. THE DECOMPOSITION OF METHYLENE DIACETATE, METHYLENE DIPROPIONATE, AND METHYLENE DIBUTYRATE[1]

By C. C. Coffin[2] and W. B. Beazley[3]

Abstract

The homogeneous decomposition of methylene diacetate vapor to formaldehyde and acetic anhydride at temperatures between 220° and 305° C. and at pressures ranging from several centimetres of mercury to several atmospheres has been studied. Reaction rates were determined by analytical and by pressure change methods. The first order decomposition is opposed by a second order recombination. A secondary reaction makes it impossible to determine the exact position of the resulting equilibrium. Within the rather large experimental error, methylene diacetate has the same activation energy (33,000 cal.) as its homologues. Its specific reaction velocity is smaller than that of the ethylidene esters. Methylene dipropionate and dibutyrate decompose at the same rate as the diacetate. These facts are in accord with the hypothesis that the extent to which a radical can contribute to the energy of activation is dependent upon its position in the molecule. Veolcity constants are given by the equation $k = 1.7 \times 10^9\, e^{-\frac{33000}{RT}}$.

Introduction

It has been shown in previous papers of this series (1, 2, 3) that esters represented by the formula $RCH(OOCR')_2$ decompose homogeneously in the gaseous state giving an aldehyde and an acid anhydride. The reaction, which takes place at a measurable velocity at temperatures between 200° and 300° C., is of the first order, and may be followed by rate of change of pressure at constant volume. It should be emphasized that the relatively low temperatures at which these decompositions attain a measurable rate eliminates the possibility of any free-radical chain mechanism, so that in all probability the primary reaction is a truly unimolecular process (6).

The general trend of the data already published (5) may be briefly summarized. Within experimental error the activation energy is a constant for the series. The addition of $-CH_2-$ groups to the aldehyde side (R) of the ester results in an increase in reaction rate, while such an addition to the hydrocarbon chains on the anhydride side (R') has little or no effect.

These data led to the use of the following hypothesis (2, 5) as a guide to further investigation. Energy can pass into a potentially reactive bond more readily from some parts of the molecule than from others. If the size and therefore the energy capacity of the part in good communication with this bond be increased, there will be an increased probability that this bond will acquire the energy necessary for its disruption. On the other hand, an increase

of complexity in a part of the structure which is "insulated" from the reactive bond should not influence the chance of sufficient energy finding its way to the weak point of the molecule. From this obviously over-simplified point of view it would seem that the $-CH_2-$ groups on the anhydride side of the ester molecules do not easily exchange energy with the breaking bonds. The atoms on the aldehyde side, however, may act as energy reservoirs for the reaction.

As the constant activation energy and the wide variety of structural alterations possible in this series of compounds seemed to afford a good opportunity for studying the effect of molecular constitution on reaction velocity, a systematic search for empirical regularities was undertaken.

The present paper deals with the decomposition of methylene diacetate, dipropionate and dibutyrate to formaldehyde and the acid anhydrides. The activation energy is approximately the same as that previously found for other members of the series. The specific reaction velocity at any temperature is, as the above hypothesis would predict, smaller than that of esters made from higher aldehydes. Methylene dipropionate and methylene dibutyrate react at the same rate and with the same activation energy as methylene diacetate, so that here also the foregoing hypothesis receives experimental support.

An interesting feature of the methylene ester decompositions is that they do not go to completion at ordinary pressures, but proceed to a measurable equilibrium where the velocity of the second order recombination is equal to that of the first order decomposition.

Experimental

Ester Preparation

Methylene diacetate was prepared by absorbing formaldehyde vapor in hot acetic anhydride containing a trace of sulphuric acid. After the catalyst had been neutralized with sodium acetate, the ester was purified by a method similar to that used in the case of butylidene diacetate (3). Three different preparations, all boiling at temperatures between 167° and 168° C., were made from formaldehyde and anhydride from different sources. All three decomposed at the same rate. The dipropionate and the dibutyrate were made by absorbing formaldehyde vapor in the respective anhydrides.

Apparatus and Technique

Reaction velocities were determined by two different methods.

(1) A weighed quantity of ester in a glass capsule was sealed inside an evacuated reaction tube the volume of which was determined after the experiment. After a known time at a definite temperature (the vapor of benzophenone boiling under a constant pressure) the tubes were removed, broken under distilled water, and analyzed for acetic anhydride.

(2) At pressures below atmospheric the rate of change of pressure at constant volume was determined in an apparatus already described (4).

For runs at pressures between 1 and 3 atm. the apparatus shown in Fig. 1 proved to be very satisfactory. Two similar tubes A and B (capacity 80–100 cc.) were joined together at the bottom by a short capillary U-tube. A three foot length of heavy barometer tubing, C, was sealed to the other end of A.
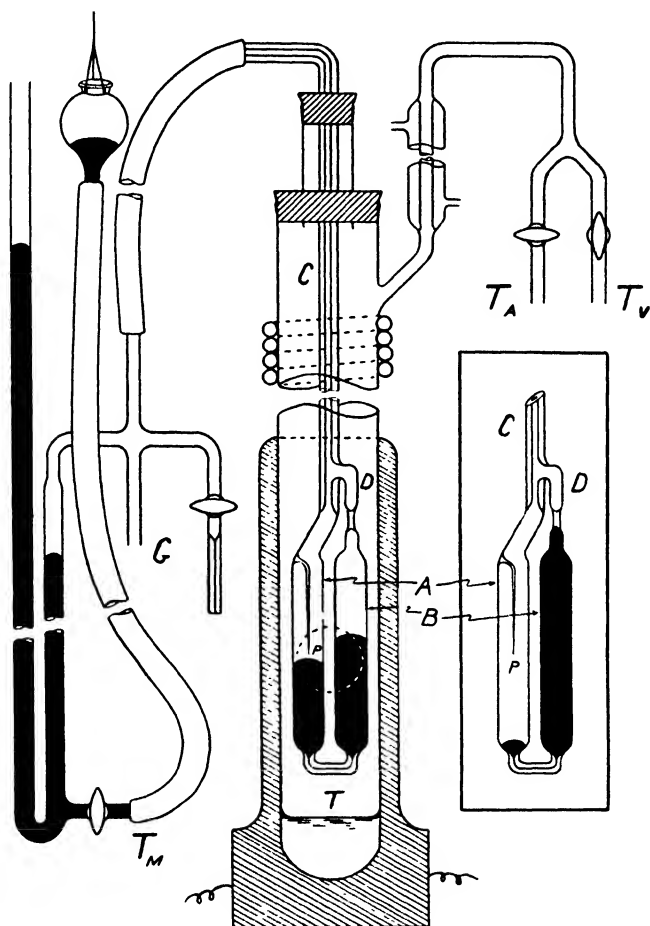
FIG. 1. *Diagram of high pressure apparatus.*

Both tubes were filled to slightly more than half their volume with distilled mercury, and a capsule containing a weighed amount of ester was dropped into the open end of B, which was then sealed to a side arm D on the tube C. When the apparatus had been evacuated (through C), D was heated and allowed to collapse so that B was separated from C. The closed tube D is left joining B and C for greater mechanical strength. A may now be opened to the atmosphere and the mercury forced into B.

To make a run, C is connected with rubber pressure tubing to a carbon dioxide cylinder (at G) and a long manometer, and the whole apparatus is

lowered into the thermostat T—a large Pyrex "test tube" containing benzo-phenone boiling at atmospheric pressure. A rubber stopper near the top of C fits tightly into the end of this tube, which can be connected through a side arm and condenser to a pump, manometer, and a 20-litre stabilizing volume. As soon as the thermostat is stoppered it is connected to this volume, and the pressure is set to that corresponding to the temperature desired. When the bulb breaks and the ester vaporizes, the pressure in A is adjusted by means of the carbon dioxide cylinder until the mercury surface is at the pointer P, where it is kept throughout the reaction, which is followed by the rate of pressure increase.

Results

In Fig. 2 the percentage reaction in one hour at 290° C. as determined by analysis is plotted against calculated initial pressure. The decrease in decomposition with increase of pressure suggests that the reaction does not go to completion. That this is actually the case is evident from Fig. 3. in which percentage reaction at 279° C. is plotted against time. The lower curve represents the ester decomposition, and the upper curve, the percentage
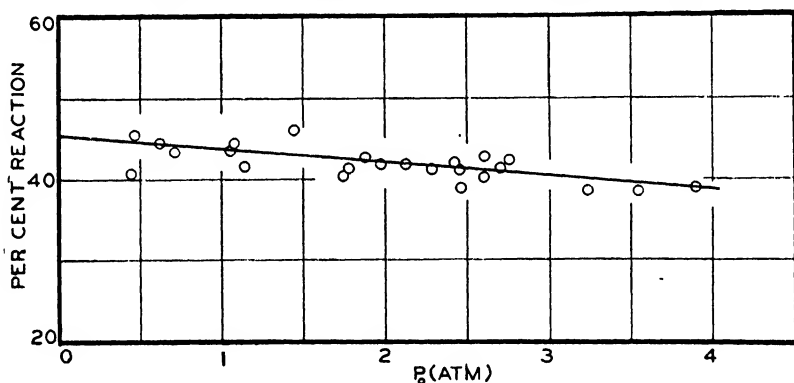
FIG. 2. *Percentage reaction in one hour at 290° C.*
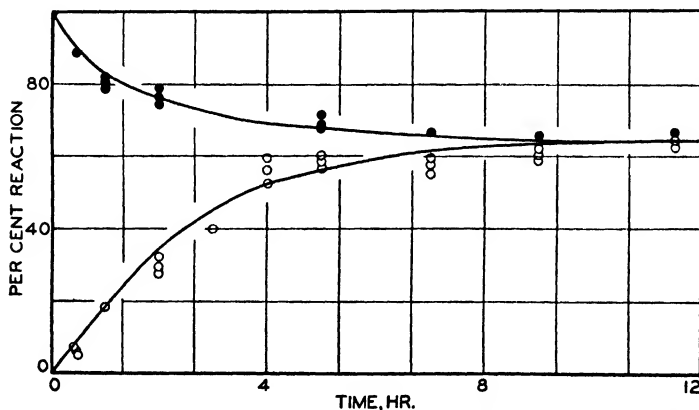
FIG. 3. *The system formaldehyde-acetic anhydride-methylene diacetate. Temp., 279° C. Equilibrium pressure, about 5 atm.* ●, *Association.* ○, *Dissociation.*

reaction in an equimolecular mixture of formaldehyde and acetic anhydride. Reactant quantities and bulb volumes were such that the final equilibrium pressure in each case would have been between 5 and 6 atm. The existence of a true equilibrium corresponding under these conditions to about 35 mole per cent ester is unmistakable.

The determination of the decomposition velocity constants by rate of pressure change is somewhat complicated by the presence of this reverse reaction. A more troublesome correction arises from the fact that a consecutive reaction (probably a heterogeneous decomposition of formaldehyde) prevents the system from reaching a steady final pressure. The following method was finally adopted for estimating velocity constants from observed pressure changes.

The reaction being of the type $AB \rightleftarrows A + B$, the velocity equation will be

$$- \frac{d[AB]}{dt} = k_1[AB] - k_2[A][B] \ .$$

If the partial pressures of ester aldehyde and anhydride expressed in terms of total pressure, P, and initial pressure, P_0, are substituted for concentrations, the expression becomes

$$\frac{dP}{dt} = k_1(2P_0 - P) - k_2(P - P_0) \ .$$

Substituting Kk_1 for k_2 and integrating, we have

$$k_1 = \frac{2.3K}{Ct} \log \frac{(P - 3P_0)K - (P - P_0)C}{(P - 3P_0)K + (P - P_0)C} \ ,$$

where K is the equilibrium constant and $C = \sqrt{K^2 + 4P_0K}$.

The fact that the system does not reach a steady final pressure makes it impossible to determine K directly. An indirect estimation of sufficient accuracy for the present purpose may be obtained from a consideration of the rate, k', at which the system moves toward equilibrium. This rate is given by the equation

$$k' = k_1 + k_2 = \frac{2.3}{t} \log \frac{P_F - P_0}{P_F - P} \ ,$$

where P_F is the final equilibrium pressure. The true value of P_F may be taken as that value (determined by trial and error) which will make the graph of $\log \frac{P_F - P_0}{P_F - P}$ against time a straight line over the first 50 to 60% of the reaction. This calculated P_F is used to evaluate K, and hence k_1 and k_2. The large uncertainty in the equilibrium constant obtained in this way is not so serious in the velocity constant where K appears as a correction term.

Many unsuccessful attempts were made to find a catalyst for the reaction in order to determine K directly and more accurately over a wider temperature range. The presence of mercury, glass surface, oxygen, water vapor, hydrogen chloride, sulphur dioxide, or iodine was found to have no measurable effect on the reaction rate as determined by analysis. A greenish brown

fluorescent film formed slowly on the walls of the reaction tubes whether or not a "catalyst" was present, and in most of the bulbs a few cubic centimetres of a water insoluble gas was formed.   Several microanalyses showed this gas to be mostly carbon monoxide and hydrogen, so that the consecutive reaction interfering with the velocity and equilibrium measurements is probably a heterogeneous decomposition of formaldehyde or of one of its polymers.

While any one experiment gave fairly consistent rate constants, the results of different runs are so scattered that it is sufficiently precise to report the data graphically.   Fig. 4 shows the total pressure plotted against time for
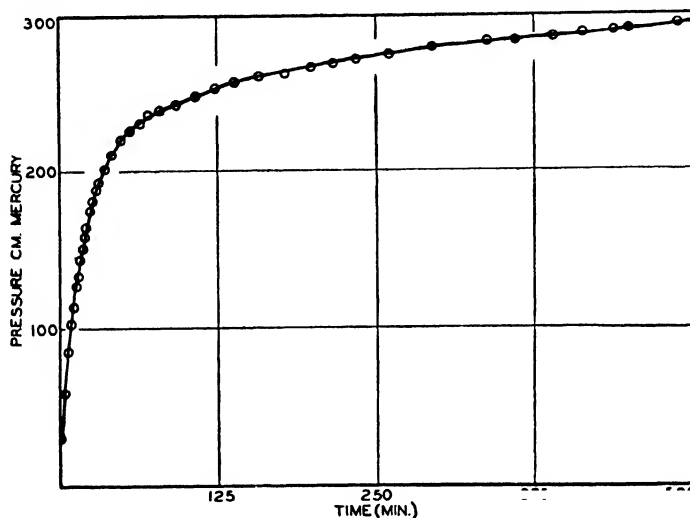
FIG. 4.   *Data of typical methylene diacetate run.*

a typical run (made with the apparatus of Fig. 1; methylene diacetate, $P_0 = 115$ cm. of mercury; $T = 579°$ C.)   The time axis is compressed to indicate the difficulty of determining the true final pressure.   In Fig. 5, which includes the results of all the 60 runs on the three esters made by pressure
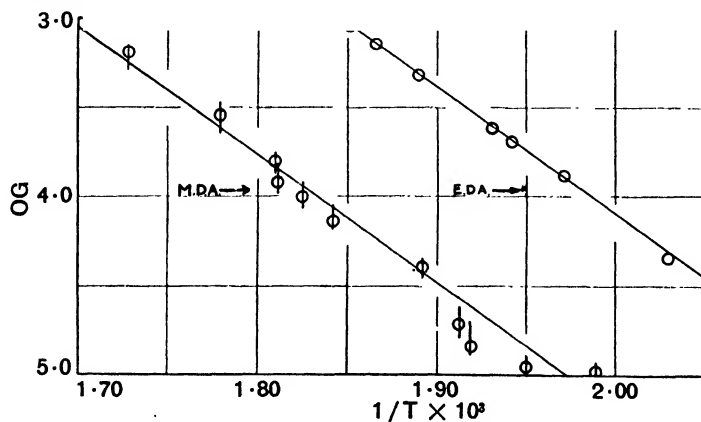
FIG. 5. $-log\ k_1$ *plotted against* $1/T$.

change methods, $-\log k$ is plotted against $1/T$. The lower line refers to the methylene esters, while the upper represents the previously determined (2) data for ethylidene diacetate. The methylene points give the mean of the results at the respective temperatures. The vertical lines through the points indicate the range covered by these results. Initial pressures varied from 0.1 to about 3 atm.

The straight line through the methylene points has arbitrarily been given the same slope as that through the ethylidene points. It is evident that within the unfortunately large experimental error of from 10 to 20%, the activation energies are the same. On account of the fact that the uncertainties due to incomplete decomposition and the consecutive reaction probably vary widely with both pressure and temperature, it is impossible, without the statistical treatment of an inconveniently large number of experimental results, to estimate the errors with any degree of accuracy. All that can be said with certainty at present is that methylene diacetate, dipropionate, and dibutyrate decompose at rates and with activation energies that are practically identical. This reaction rate is about $\frac{1}{12}$ that of ethylidene diacetate at any temperature. The straight lines of Fig. 5 are given by the following equations.

$$\text{Ethylidene diacetate:} \qquad k = 2 \times 10^{10} e^{-\frac{33000}{RT}}$$

$$\text{Methylene diacetate, etc.:} \quad k = 1.7 \times 10^{9} e^{-\frac{33000}{RT}}$$

In connection with the reverse reaction, it is of interest to attempt an estimate of the proportion of "activated" collisions that result in the formation of ester molecules. This amounts to determining the factor P in the equation $k_2 = PZe^{-E/RT}$, where Z is the number of collisions. At 562° C. the equilibrium constant in atmospheres, Kp, has a value of about 2 for methylene diacetate. (Kp is appreciably smaller in the case of the dipropionate and the dibutyrate.) If atmospheres are converted to moles per litre, the constant, K, becomes 0.04, which makes k_2 equal to 7×10^{-3} litres mole^{-1} sec^{-1}. ($k_1 = 3 \times 10^{-4}$ sec^{-1}.) The heat of reaction is unknown (the values of Kp are too uncertain to permit calculation of ΔH), but is probably about 6000 cal. per mole, so that $E_2 = 33,000 - 6000 = 27,000$ cal. approximately. If a mean molecular diameter of 5×10^{-8} cm. is assumed, it is found that k_2 should be about 11 if every collision between activated molecules results in reaction. It thus appears that P is roughly 10^{-3}, or that only about 1 in every 1000 collisions between activated formaldehyde and acetic anhydride molecules leads to ester formation. This preponderance of unfruitful collisions is probably due to the necessity of fulfilling some rather exacting conditions of orientation or phase synchronism at the moment of impact. It is perhaps significant that the A-factor of the first order decomposition is also smaller by about 10^3 than that usually found experimentally for unimolecular reactions, or calculated from Rice and Gershinowitz' hypothesis of "exact orientation" (7). A detailed investigation of the association reaction is in progress.

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THE DECOMPOSITION OF NITROUS OXIDE ON A SILVER CATALYST[1]

By E. W. R. Steacie[2] and H. O. Folkins[3]

Abstract

The kinetics of the thermal decomposition of nitrous oxide on a silver catalyst has been investigated. The rate of the reaction can be expressed by the equation

$$- \frac{d}{dt} (N_2O) = \frac{K(N_2O)}{1 + b(O_2)} .$$

It may therefore be concluded that the nitrous oxide is slightly adsorbed by the catalyst, while oxygen is fairly strongly adsorbed and retards the reaction. Added oxygen affects the reaction in the manner predicted by the rate equation, in contrast to its behavior on a platinum catalyst as previously found by Steacie and McCubbin.

Introduction

The retardation of a reaction by its products constitutes an important phase of heterogeneous catalysis. The explanation of this retardation lies unquestionably in preferential adsorption of the products of reaction, which thus reduce the space available for the adsorption of the reactant.

Comparatively few heterogeneous gas reactions, however, have been thoroughly investigated from this point of view. Of these, the most thoroughly investigated is the decomposition of nitrous oxide on the surface of platinum. The reaction is

$$N_2O = N_2 + \tfrac{1}{2}O_2 ,$$
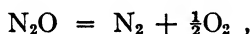
and it is retarded by the oxygen formed. Hinshelwood and Prichard (3) first investigated the reaction, using electrically heated filament catalysts at temperatures between 600° and 1200° C. They found that added oxygen had the same retarding effect as oxygen formed during the reaction, and that the rate could be expressed by

$$- \frac{d}{dt} (N_2O) = \frac{K(N_2O)}{1 + b(O_2)} . \tag{1}$$

Schwab and Eberle (6) investigated the reaction in a similar way, but came to the conclusion that added oxygen had no retarding effect.

Low pressure measurements were also made by Cassel and Glückauf (2) and by van Praagh and Topley (5).

In view of the disagreement regarding the mode of action of added oxygen, a thorough investigation of the reaction on a platinum sponge catalyst was made by Steacie and McCubbin (13, 14). The main facts established by their investigation were:

(1) Oxygen formed in the reaction retards it, the rate being given by Equation (1).

(2) Oxygen added to the reaction mixture diminishes K, and thus retards the reaction. (O_2) in the denominator, however, refers only to oxygen formed in the reaction, and not to oxygen added initially.

(3) Adsorption measurements show no appreciable difference between the adsorption of oxygen formed in the reaction and that of oxygen added initially. It may therefore be concluded that at least the major portion of the oxygen formed in the reaction is not irreversibly adsorbed.

(4) The reversibility of the adsorption process is further confirmed by the fact that the amount of oxygen adsorbed is not altered by evacuation at a red heat, or by preliminary burning off with hydrogen. It is also confirmed by the fact that in reaction rate experiments the time of evacuation has no effect on the rate of the following run.

Two of the above facts stand out as quite irreconcilable, *viz.*, (i) oxygen can retard the reaction in two different ways, (ii) the adsorption process is rapidly reversible. "Now it should be noticed that the rate equation given above, in the case where (O_2) refers only to oxygen formed in the reaction, is really of the form

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + f(\text{amount of } N_2O \text{ decomposed})}$$

It is therefore possible that the retardation of the reaction by oxygen formed in it is partly real (inasmuch as added oxygen retards it also), but is mainly fictitious and due merely to the fact that f(amount of N_2O decomposed) is identical with f(amount of O_2 formed). Hence the retardation of the reaction by any other substance produced in it would be indistinguishable from retardation by oxygen." Steacie and McCubbin therefore concluded that the retardation of the reaction was probably due to a trace of some substance formed in a side reaction.

In view of the peculiar results obtained with platinum it appears to be worth while to investigate the oxygen retardation on other catalysts. The decomposition has been investigated on gold (4), but it is not retarded by oxygen. It has also been thoroughly investigated on oxide catalysts by Schwab and his co-workers (7, 8, 9, 10, 11), but the results are hardly comparable with those obtained on metal surfaces. The reaction has also been investigated on a silver catalyst by Benton and Thacker (1). This work, however, was only incidental in the course of another investigation, and no

conclusions as to oxygen retardation can be drawn from their results. It therefore seemed worth while to investigate the reaction on a silver catalyst more thoroughly from the point of view of the effect of oxygen on the rate.

Experimental

Reaction velocities were followed by observing the rate of change of pressure in a system at constant volume. The reaction vessel was made of Pyrex glass and had a capacity of about 175 cc. The pressure was measured with a capillary mercury manometer. The apparatus was similar to the general type that has been used in this laboratory in a number of previous investigations (12). The required temperatures were obtained by means of an electric furnace, and the temperature was measured with a chromel-alumel thermocouple in conjunction with a potentiometer. The temperature was controlled by manual regulation and could be maintained constant to within 2°.

Prior to making a run the system was evacuated to about 10^{-4} mm. by means of a mercury vapor pump backed by an oil pump. The time of evacuation was found to have no apparent effect upon the rate of the following run.

The silver catalyst was prepared by the method of Benton and Thacker. Finely divided precipitated silver oxide was slowly reduced by hydrogen over a period of 12 hr. at a temperature ranging from 25° C. at the start to 100° C. at the end. The silver oxide was prepared by precipitation from a solution of silver nitrate by the addition of barium hydroxide, the precipitation being carried out in the absence of carbon dioxide. Approximately 30 gm. of catalyst was used. Care was taken to keep the catalyst out of contact with air between experiments.

Nitrous oxide was obtained in cylinders from the Ohio Chemical and Manufacturing Co. It was fractionally distilled and stored in a large reservoir. Oxygen was obtained from commercial cylinders, and was used without purification except for drying.

Experimental Results

The catalyst was sufficiently active to produce appreciable decomposition at 375° C. It was, however, not found possible to produce as active a catalyst as that of Benton and Thacker, who were able to detect decomposition at the surprisingly low temperature of 60° C. Since the main object of this work was to investigate the effect of oxygen on the rate of the reaction, all runs were made at one temperature, *viz.*, 450° C. This temperature was chosen because the reaction proceeded at the most conveniently measurable rate. The rate of the homogeneous decomposition at 450° C. is negligibly slow, so that no complications are introduced on this account.

The catalyst showed signs of aging during the first four or five runs. After this its activity was reasonably constant.

I. The Decomposition of Pure Nitrous Oxide

The data for two typical runs are given in Tables I and II. In the tables, P represents the total pressure at any time, while x is the amount of nitrous oxide which has reacted. In calculating x it is necessary to know the total increase in pressure corresponding to complete reaction. The results of this, and of other investigations, indicate that the full 50% pressure increase corresponding to the equation $N_2O = N_2 + \frac{1}{2}O_2$ is not quite attained in practice. Allowing for this, and for the correction due to the dead space, we have assumed, throughout, that completion corresponds to a pressure increase of 45%. A slight change in this value would have no appreciable effect on the conclusions to be drawn. It will be seen from the tables that the rate of the reaction is very high at the start and that it falls off rapidly, thus suggesting retardation by the products of the reaction. For a reaction in which the reactant is slightly adsorbed and the products are moderately strongly adsorbed, we get an equation of the form which has already been shown to hold for the nitrous oxide decomposition on platinum, viz.,

TABLE I

DATA FOR A TYPICAL RUN

Time, min.	P, cm.	x, cm.	K_m	V
0	9.38	—	—	—
1	10.25	1.91	0.0989	1.91
2	10.88	3.30	0.0942	1.65
3	11.22	4.05	0.0818	1.35
4	11.52	4.71	0.0757	1.18
5	11.78	5.28	0.0718	1.05
6	12.00	5.76	0.0689	0.96
8	12.36	6.56	0.0670	0.82
10	12.62	7.13	0.0620	0.71
15	12.96	7.88	0.0531	0.52
20	13.24	8.49	0.0461	0.42

TABLE II

DATA FOR A TYPICAL RUN

Time, min.	P, cm.	x, cm.	K_m	V
0	29.00	—	—	—
1	30.46	3.21	0.0510	3.21
2	31.73	6.00	0.0503	3.00
3	32.60	7.92	0.0461	2.64
4	33.45	9.79	0.0447	2.45
5	34.12	11.26	0.0426	2.25
7	35.12	13.46	0.0387	1.92
9	35.88	15.14	0.0356	1.68
11	36.54	16.59	0.0335	1.51
14	37.24	18.13	0.0304	1.29
20	38.50	20.90	0.0277	1.04
25	39.24	22.53	0.0261	0.90

$$-\frac{d}{dt}(N_2O) = \frac{K(N_2O)}{1 + b(O_2)} = \frac{K(a - x)}{1 + bx} ,$$

where a is the initial concentration of the reactant. On integration this gives

$$K = \frac{1 + ab}{t} \ln \frac{a}{a - x} - \frac{bx}{t} .$$

If (3)

$$\frac{1}{t} \ln \frac{a}{a - x} = K_m , \quad \text{and} \quad \frac{x}{t} = V,$$

this becomes

$$V = (a + 1/b)K_m - K/b . \tag{2}$$

Hence, a test of the applicability of the equation may be made by plotting K_m against V, and seeing whether a straight line is obtained. This has been done for several runs, and the curves are shown in Fig. 1. The linearity is
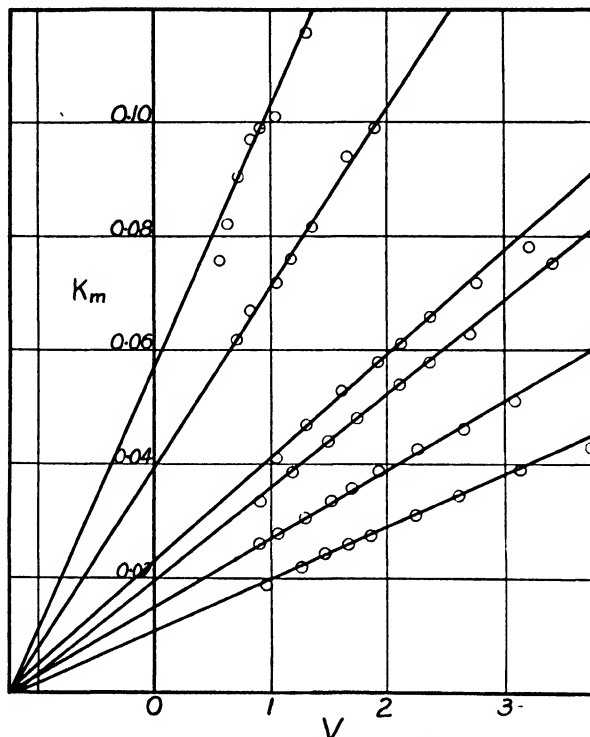
FIG. 1. *Pure nitrous oxide.*

excellent, and there is no doubt that Equation (2) fits the results. It may therefore be concluded that the reaction is retarded by oxygen on a silver surface in the same manner as on a platinum surface.

From Equation (2) we obtain for the time to one-half value

$$t_{50} = \frac{0.69}{K} + \frac{0.19\,ab}{K}.$$

Hence, if the equation fits the data over the concentration range we should obtain a straight line on plotting t_{50} against a, from the slope and intercept of which we can evaluate both b and K for the given temperature and catalyst. Table III gives the values of t_{50} for various initial pressures of nitrous oxide.

TABLE III
EFFECT OF PRESSURE ON THE RATE OF REACTION

t_{50}, min.	P, cm.	t_{50}, min.	P, cm.	t_{50}, min.	P, cm.
7.5	10.50	4.2	9.85	6.5	21.40
3.0	5.55	7.4	29.12	4.0	9.38
11.5	39.70	3.8	9.50	5.2	19.60
11.0	32.60	8.1	29.00	6.0	18.70
7.8	19.90	4.7	9.30	4.5	10.08
10.1	28.60				

The data are listed in the order in which the runs were made. Some drift is apparent in the earlier runs.

In Fig. 2, t_{50} is plotted against the initial pressure. From the intercept and slope of the line we get

$$K = 0.383 , \qquad b = 0.500 .$$

Hence the rate of reaction may be expressed by

$$-\frac{d}{dt}(N_2O) = \frac{0.383(N_2O)}{1 + 1.10(O_2)} . \tag{3}$$

It remains to be seen whether this will also fit the results in experiments in which oxygen has been added initially.
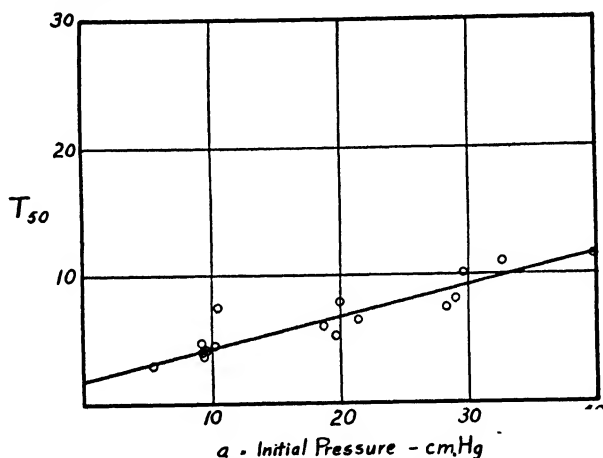
FIG. 2. *The effect of pressure on the decomposition of pure nitrous oxide.*

II. The Effect of Added Oxygen

It is apparent that if added oxygen affects the rate in the manner indicated by Equation (3), then high oxygen concentrations should be able to swamp out the effect of the oxygen formed in the reaction. The denominator will then become constant for a given run, and the rate will be given by

$$-\frac{d}{dt}(N_2O) = K_1(N_2O) .$$

In other words the retarding effect of the oxygen will become constant throughout an experiment and the reaction will now follow a first order equation. Data for typical runs in the presence of a large amount of added oxygen are given in Table IV, and the results of a number of such runs are given in Fig. 3 in the form of a $\ln \dfrac{a}{a - x} - t$ plot.

It will be seen that quite good first order constants are obtained. We may therefore conclude that added oxygen retards the reaction in the same way as does oxygen formed in it. Whether added oxygen is as efficient as

TABLE IV
TYPICAL EXPERIMENTS WITH LARGE AMOUNTS OF ADDED OXYGEN

	Initial N_2O pressure							
	8.31 cm.					7.38 cm.		
	Initial O_2 pressure							
	32.24 cm.					27.92 cm.		
Time, min.	P, cm.	x, cm.	K_m		Time, min.	P, cm.	x, cm.	K_m
0	40.55	—	—		0	35.30	—	—
1	40.65	0.22	0.0117		1	35.45	0.33	0.0199
2	40.72	0.37	0.0099		2	35.56	0.57	0.0175
3	40.80	0.55	0.0099		3	35.66	0.79	0.0164
5	41.00	0.99	0.0110		5	35.85	1.21	0.0156
7	41.18	1.39	0.0113		7	36.04	1.63	0.1054
10	41.46	2.00	0.0119		10	36.33	2.27	0.0159
12	41.65	2.42	0.0124		15	36.68	3.04	0.0154
14	41.82	2.79	0.0127		20	36.92	3.56	0.0143
16	41.96	3.10	0.0128		25	37.14	4.05	0.0138
20	42.28	3.81	0.0133		30	37.38	4.58	0.0140
24	42.48	4.25	0.0129		40	37.64	5.15	0.0130
30	42.72	4.77	0.0123					
50	43.40	6.27	0.0122					
70	43.70	6.93	0.0117					

that formed in the reaction in causing its retardation still requires investigation. In order to test this point runs were made with successively smaller amounts of added oxygen. Fig. 3 also shows the results of two runs with a 1 to 1 oxygen-nitrous oxide mixture, and the data for two typical runs of this type are given in Table V.

It will be seen from Table V that, while there is a certain amount of drift of the constants, the reaction is still virtually first order, the added oxygen being still sufficient to swamp out the effect of the oxygen formed in the reaction. Experiments were therefore made with very small amounts of added oxygen, and the results are given in Table VI for two typical cases. It will be seen that the reaction is no longer even approximately first order. A $K_m - V$ plot of these runs is given in Fig. 4, from which it may be seen that the linearity is excellent.
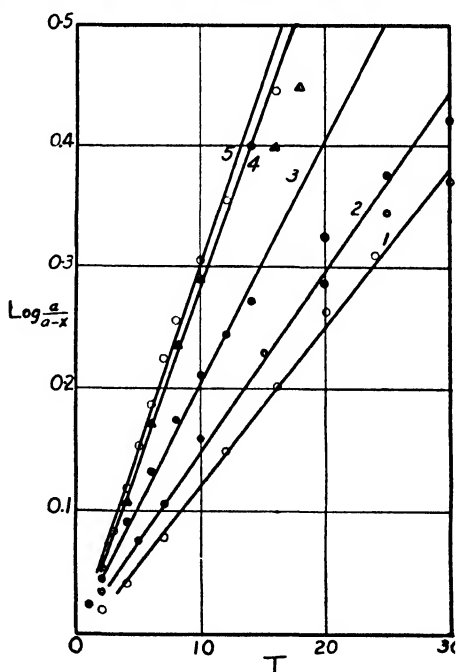
FIG. 3. *Experiments with large amounts of added oxygen. Curves 1, 2, and 3 for runs with a 4 O_2 : 1 N_2O mixture. Curves 4 and 5 for runs with a 1 O_2 : 1 N_2O mixture.*

TABLE V

Experiments with approximately 1 : 1 N_2O — O_2 mixtures

Initial N_2O pressure								
8.27 cm.			‖	5.85 cm.				
Initial O_2 pressure								
8.83 cm.			‖	6.25 cm.				
Time, min.	P, cm.	x, cm.	K_m	Time, min.	P, cm.	x, cm.	K_m	
0	17.10	—	—	0	12.10	—	—	
1	17.34	0.53	0.0288	1	12.38	0.62	0.0487	
2	17.54	0.97	0.0271	2	12.60	1.10	0.0452	
3	17.74	1.41	0.0271	3	12.85	1.65	0.0480	
4	18.00	1.98	0.0297	4	13.04	2.08	0.0499	
6	18.42	2.90	0.0312	5	13.26	2.55	0.0497	
8	18.76	3.65	0.0316	6	13.44	2.95	0.0508	
10	19.00	4.18	0.0306	8	13.72	3.56	0.0509	
12	19.20	4.62	0.0296	10	13.90	3.96	0.0491	
14	19.36	4.97	0.0285	14	14.16	4.53	0.0465	
18	19.66	5.63	0.0276	18	14.38	5.02	0.0471	
22	19.90	6.16	0.0270	25	14.56	5.46	0.0470	
26	20.09	6.58	0.0269					
35	20.40	7.04	0.0237					

TABLE VI

Experiments with small amounts of added oxygen

Initial N_2O pressure									
20.51 cm.				‖	9.20 cm.				
Initial O_2 pressure									
5.34 cm.				‖	2.40 cm.				
Time, min.	P, cm.	x, cm	K_m	V	P, cm.	x, cm.	K_m	V	
0	25.85	—	—	—	11.60	—	—	—	
0.5	26.70	1.87	0.0832	3.74	12.12	1.14	0.1150	2.28	
1	27.45	3.52	0.0818	3.52	12.62	2.24	0.1212	2.24	
1.5	28.10	4.95	0.0800	3.30	13.00	3.08	0.1180	2.05	
2	28.65	6.16	0.0776	3.08	13.28	3.70	0.1117	1.85	
3	29.70	8.47	0.0771	2.82	13.70	4.62	0.0976	1.54	
4	30.44	10.10	0.0721	2.52	14.08	5.46	0.0977	1.36	
5	31.02	11.37	0.0701	2.27	14.36	6.07	0.0936	1.21	
6	31.50	12.43	0.0674	2.07	14.56	6.51	0.0890	1.08	
8	32.24	14.06	0.0628	1.75	14.85	7.15	0.0815	0.89	
10	32.74	15.16	0.0584	1.52	15.04	7.57	0.0752	0.76	
12	33.12	15.99	0.0547	1.33	15.14	7.79	0.0679	0.65	
14	33.36	16.52	0.0508	1.17	15.24	8.01	0.0634	0.57	
18	33.76	17.40	0.0455	0.97	15.32	8.18	0.0531	0.45	
22	33.98	17.89	0.0406	0.81	—	—	—	—	
30	34.18	18.33	0.0324	0.61	15.46	8.49	0.0371	0.28	
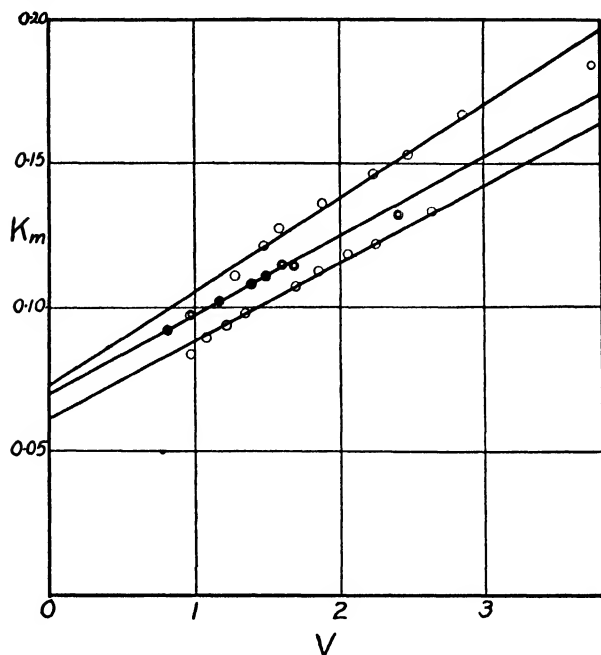
FIG. 4. *Experiments with small amounts of added oxygen.*

If y is the concentration of added oxygen, the other symbols having the same meaning as before, the rate equation becomes

$$\frac{dx}{dt} = \frac{K(a - x)}{1 + b(x + 2y)} ,$$

which on integration gives

$$\frac{(1 + 2by + ab)}{t} \ln \frac{a}{a - x} - \frac{bx}{t} = K .$$

Whence

$$V = (a + 2y + 1/b)K_m - K/b .$$

Hence V should be a linear function of K_m, the intercept being $-K/b$ as before.   The slope, however, is now $(a + 2y + 1/b)$ instead of $(a + 1/b)$. Fig. 4 shows that K_m plotted against V gives straight lines.

Unfortunately the runs in Table VI and Fig. 4 are not strictly comparable with the preceding runs, inasmuch as they were done with a new catalyst, the former one having been accidently damaged.   Experiments showed that the new catalyst had an activity about 1.80 times greater than the former (*i.e.* K was 1.80 times larger, *viz.*, 0.69), but that the constant b was unchanged.   Thus for a number of runs with pure nitrous oxide with the new catalyst, using $K = 0.69$, and the previous value of b, we have

P, cm.	7.9	10.7	30.0	10.1	19.6
t_{50}, obs.	2.2	2.2	5.1	2.2	3.0
t_{50}, calcd.	2.1	2.5	5.0	2.4	3.3

The simplest way of checking the efficiency of the added oxygen in retarding the reaction is to calculate t_{50} and compare the result with experiment. In the presence of added oxygen we have

$$t_{50} = \frac{0.69}{K} + \frac{0.19ab}{K} + \frac{2 \times 0.69by}{K} \; .$$

Hence for the new catalyst we have

$$t_{50} = 1 + 0.138a + 1.0y \; ,$$

and for the old

$$t_{50} = 1.8 + 0.252a + 1.8y \; .$$

Whence for the experiments listed in Tables IV, V, and VI we have

Experiment	Table IV	Table V	Table VI
t_{50}, obs.	22.5, 22.0	10.0, 6.0	4.2, 3.0
t_{50}, calcd.	62.1, 53.8	19.8, 14.6	9.2, 4.7

Of course, on account of the unavoidable fluctuations in activity which occur in all catalytic investigations, a very close agreement between the observed and calculated values of t_{50} is hardly to be expected. There is, however, no doubt that the observed values of t_{50} in the presence of added oxygen are considerably lower than those calculated. In other words, added oxygen is not as efficient in retarding the reaction as is that formed in it, by a factor of 2 or 3. Inasmuch as oxygen formed in the reaction is adsorbed at the moment of its formation, it is evident that a slight time lag before desorption could cause temporary supersaturation of the surface and explain the observed effect. Such a time lag is, in fact, to be expected.

It may therefore be concluded that added oxygen affects the rate in the manner indicated by the rate equation, but is not quite as efficient as oxygen formed in the reaction. There are, however, no peculiarities of the type observed in the decomposition on a platinum catalyst.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

VII. THE DECOMPOSITION OF ETHYLIDENE DIBUTYRATE AND HEPTYLIDENE DIACETATE[1]

By C. C. Coffin[2], J. R. Dacey[3] and N. A. D. Parlee[4]

Abstract

Ethylidene dibutyrate and heptylidene diacetate decompose in the vapor state at temperatures between 200° and 300° C. to form an aldehyde and an anhydride. The reactions are homogeneous, unimolecular, and complete. The activation energy is the same as that previously found for other members of this homologous series. Ethylidene dibutyrate decomposes at the same rate as ethylidene diacetate, and thus provides further evidence that the specific reaction velocity is independent of the size of the anhydride radicals. Heptylidene diacetate decomposes at the same rate as butylidene diacetate. This indicates that after the aldehyde radical has attained a certain size (three or four carbon atoms) the addition of $-CH_2-$ groups leaves the specific reaction velocity unchanged. The velocity constants are given by the equations

$$\text{ethylidene dibutyrate, } k = 1.8 \times 10^{10} \, e^{-\frac{33000}{RT}},$$

$$\text{heptylidene diacetate, } k = 3.0 \times 10^{10} \, e^{-\frac{33000}{RT}}.$$

Introduction

A study of the thermal decomposition of ethylidene diacetate homologues has been undertaken for reasons already outlined (1, 4, 5). This paper is concerned with the breakup of ethylidene dibutyrate and heptylidene diacetate —the largest purely aliphatic molecules of this series yet investigated. These esters resemble their homologues in that their vapor phase decomposition is unimolecular and homogeneous, and goes to completion at pressures up to atmospheric. Within experimental error, the activation energies are identical with those found for other members of the series. Ethylidene dibutyrate at any temperature decomposes at the same rate as ethylidene diacetate. The specific reaction velocity of heptylidene diacetate is somewhat greater than this, and is practically the same as that of butylidene diacetate. These data are thus further evidence that additions to the anhydride side of the molecule are without influence on the decomposition velocity. It appears also that after the butylidene radical is reached, no velocity increment accompanies the addition of $-CH_2-$ groups to the aldehyde side. In this respect the chemical behavior parallels the well known tendency of many physical properties to reach the limiting value of the series with the four carbon member.

It is worth emphasizing that the reaction is of such a type and occurs over such a temperature range that the observed rate is almost certainly that of the primary unimolecular step.

Experimental

Preparation of Esters

The esters were prepared by heating equimolecular quantities of the respective aldehydes and anhydrides in the presence of a trace of sulphuric acid. The products were washed with sodium acetate solution, dried with calcium chloride, and fractionated by vacuum distillation. Their identity and purity were established by saponifications and molecular weight determinations.

Rate Measurements

Two independent pieces of apparatus (volumes of reaction chambers were 1020 and 384 cc.) of a type already described (3) were used for most of the reaction velocity measurements. For each ester the pressure increase was quite accurately 100%. In a few experiments carried out in bulbs the percentage reaction in a known time at a known temperature was determined by analysis of the reaction products.

Results

The experimental results are summarized in Table I. The initial pressures given in Column 3 are calculated by means of the gas laws from the weight

TABLE I

SUMMARY OF REACTION VELOCITY DATA

Run No.	$T°$, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Ethylidene dibutyrate					
15	513.0	9.0	1.27		
16	513.0	8.7	1.40		
22	513.1		1.50		
23	513.1		1.10	3.839	0.001949
24	513.1		1.50		
25	513.1		1.00		
27	512.9		2.25		
1	515.2	8.9	1.71	3.768	0.001941
2	515.2	13.6	1.70		
5	495.2	3.3			
8	494.4	18.2	0.451	4.346	0.002022
10	526.8	10.1	4.44		
11	526.8	10.2	4.50		
12	526.8	10.9	4.06	3.363	0.001898
13	526.9	12.2	4.32		
14	526.9	10.9	4.36		
3	539.3	9.7	9.35		
4	539.3	3.6	7.51	3.060	0.001855
6	539.3	10.3	9.34		
7	539.3	2.7	8.70		
17	563.0	27.3	27.0	2.585	0.001776
18	563.2	14.4	25.0		
19	533.2	35.7	6.80		
20	533.3	19.1	5.90	3.171	0.001876
21	533.3	35.8	7.00		
26	533.0	34.0	7.28		

TABLE I—*Concluded*

SUMMARY OF REACTION VELOCITY DATA—*Concluded*

Run No.	$T°$, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Heptylidene diacetate					
3	503.0	18.5	1.44 ⎫		
14 .	503.2	32.0	1.50 ⎬	3.873	0.001987
15	503.3	8.8	1.39 ⎭		
12	513.0	21.9	2.24 ⎫		
13	513.0	13.4	2.53 ⎬	3.616	0.001949
24	512.7	16.9	2.50 ⎭		
10	523.1	25.6	4.94 ⎫		
11	523.1	11.7	4.90 ⎬	3.311	0.001912
1	523.0	23.0	4.84 ⎭		
9	533.0	21.2	8.91 ⎫		
8	532.7	27.5	8.37 ⎬	3.048	0.001874
23	533.1	18.4	9.5 ⎬		
21	533.2	34.4	9.06 ⎭		
7	543.0	27.1	17.4 ⎫		
6	542.9	23.3	17.0 ⎬	2.775	0.001842
18	543.1	13.0	16.8 ⎬		
19	543.1	23.4	16.6 ⎭		
5	553.0	31.6	24.6 ⎫		
4	552.9	26.6	27.6 ⎬	2.554	0.001808
25	553.0	30.2	31.4 ⎭		
16	563.2	44.7	55.1 ⎫		
17	563.0	39.2	59.5 ⎬	2.260	0.001776
20	563.1	13.3	45.0 ⎬		
22	562.6	25.7	60.0 ⎭		

of ester taken. These values were usually found to be within a few milli-metres of those obtained by extrapolating the observed pressures to zero time, and to be equal, within experimental error, to one-half the final pressure. It is true that the experimental error is greater than usual on account of the fact that the low volatility of these esters necessitates a relatively high pressure of mercury vapor in the reaction chamber.

The velocity constants (Column 4) were calculated by either the Guggen-heim method (6), or by plotting log $P_o/(2P_o - P)$ against time (1).

The average value of $-\log k$ (Column 5) at each temperature is plotted against $1/T$ in Fig. 1 which, for the sake of comparison, includes the previously published data for ethylidene diacetate (1) and butylidene diacetate (2). The broken line represents the decomposition of methylene diacetate (5).

It is evident from Fig. 1 that, as far as it can be decided from these experi-ments, each ester has an activation energy of about 33,000 cal. per mole. It must be admitted that a more intensive study may reveal differences in

activation energies of sufficient magnitude to account for at least some of the observed differences in reaction rates. However, it is tentatively assumed that the exponential factor in the rate equation is a constant for this series of compounds. Such an assumption appears to be not unreasonable (see (9, p. 50)) and facilitates considerably a systematic presentation of the data.
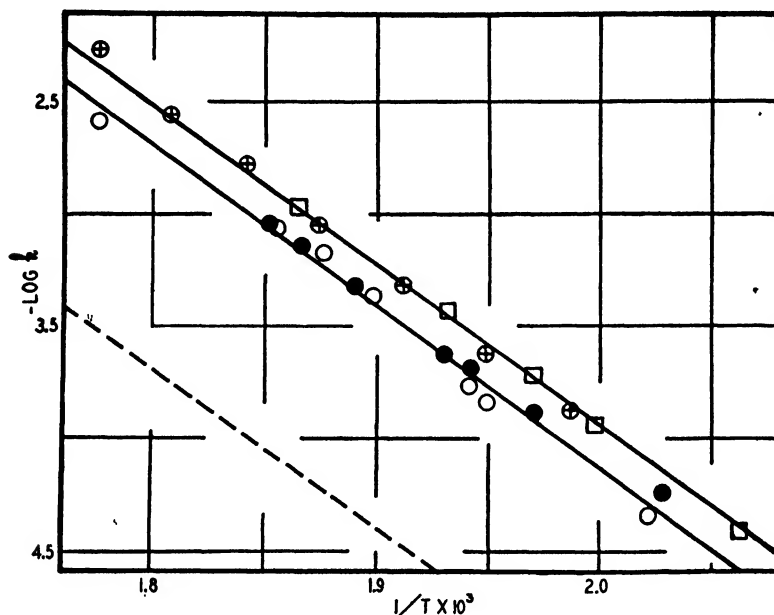
Fig. 1. $-\log k$ *plotted against* $1/T$. O, *Ethylidene dibutyrate;* ●, *ethylidene diacetate;* ⊕, *heptylidene diacetate;* □, *butylidene diacetate:* - - - -, *methylene diacetate.*

As already pointed out there is a marked difference between the reaction rates of the methylene and the ethylidene esters. The difference between those of ethylidene diacetate and butylidene diacetate is small, but it is in the same direction and is probably real. The butylidene and heptylidene compounds, however, react at the same rate at all temperatures. The ethylidene diacetate and ethylidene dibutyrate decompositions are also indistinguishable as regards rate and temperature coefficient.

Velocity constants are given by the equations:

$$\text{Ethylidene dibutyrate,} \quad k = 1.8 \times 10^{10}\, e^{-\frac{33000}{RT}},$$

$$\text{Heptylidene diacetate,} \quad k = 3.0 \times 10^{10}\, e^{-\frac{33000}{RT}}.$$

In the case of several of these esters a special effort was made to obtain a few accurate measurements under as nearly identical conditions as possible, and to discover and eliminate any catalyst that might be present. It was thought that the obscurity introduced by the uncertainty in the exponential factor of the rate expression might be avoided by such a direct comparison of the reactions at one temperature. The esters chosen were ethylidene diacetate, ethylidene dibutyrate, and butylidene diacetate. About 300 gm. of each

compound (already "purified" for reaction rate measurements) was carefully fractionated *in vacuo* through a well packed and insulated 2-ft. column. The first 5 cc. and the last 5 cc. of the distillates were collected separately, and were used for the comparative runs summarized in Table II. These runs were carried out at 253.7° C. in the large reaction chamber (volume, 1020 cc.), and every effort was made to keep conditions constant and obtain accurate readings. The temperature was unfortunately somewhat too high for the breakup of butylidene diacetate (the half-life at 253.7° C. is about 14 min.) to be followed with accuracy in this type of apparatus.

TABLE II

RATE OF DECOMPOSITION OF ETHYLIDENE DIACETATE, ETHYLIDENE DIBUTYRATE, AND
BUTYLIDENE DIACETATE AT 253.7° C.

—	Fraction	P_o, cm.	$k \times 10^4$
Ethylidene diacetate	First	17.55	4.76
	First	16.50	4.27
	Last	13.10	4.95
	Last	14.43	4.50
	Mean		4.62
	Calculated from rate equation		4.68
Ethylidene dibutyrate	First	11.13	4.24
	First	10.94	4.36
	Last	10.24	4.50
	Last	12.25	4.32
	Mean		4.36
	Calculated from rate equation		3.89
Butylidene diacetate	First	16.25	9.5
	First	15.37	8.1
	Last	12.29	9.3
	Last	14.45	8.7
	Mean		8.9
	Calculated from rate equation		7.4

It is evident from Table II that no catalyst has been concentrated in either the first or last fractions of any of the esters, so that there can be little doubt that the observed variation of the velocity constant with molecular structure is real. The agreement between the observed constants and those calculated from the previously published rate equations for ethylidene diacetate and butylidene diacetate is quite satisfactory. This indicates that the uncertainty in the activation energy is not much greater than that in determining the absolute rate. The importance of this is that the ethylidene esters have almost the same decomposition velocity, which is appreciably smaller than that of the butylidene compound.

The homogeneity of the reactions was established by experiments in which the esters were decomposed in bulbs packed with pieces of glass tubing. After a definite time in the thermostat, the contents of the bulbs was washed out and titrated with standard alkali. Changing the surface-volume ratio from 0.5 to 15 cm.$^{-1}$ caused no noticeable increase in the reaction rate.

It is of interest also that these esters decompose at the same rate in the liquid as they do in the vapor phase.   For example, the values of $k \times 10^5$ found for liquid butylidene diacetate at 210° C. were 3.5 (two hours) 2.9 (four hours) and 3.0 (six hours).   The value calculated from the rate equation of the vapor phase reaction is 3.3.   These liquid phase decompositions will be dealt with in a later paper.

Discussion

The main features of these ester decompositions may be briefly summarized. It is evident that the activation energy remains essentially constant through-out the series, so that the differences observed in the reaction velocities are probably due to variations in the non-exponential factor of the rate expression. Such behavior seems to be characteristic of homologous series, which decom-pose by a clean-cut first order mechanism (9, 10).

The effect of structural changes on the specific reaction rate is noteworthy. There is no appreciable difference between the decomposition velocities of the diacetates and the dibutyrates, so that it seems that the addition of $-CH_2-$ groups to the anhydride radicals has little or no effect on the rate of reaction.   The relative specific reaction velocities of the methylene, ethylidene, and butylidene esters at any temperature are respectively 1, 12 and 18; that is, the addition of a $-CH_2-$ group to the aldehyde radical is accompanied by a rate increase that diminishes as the series is ascended.   The fact that there is no appreciable difference between the decomposition velocities of the butylidene and heptylidene esters indicates that this effect becomes negligible after the radical has acquired more than three or four $-CH_2-$ groups.   There is thus a noteworthy difference between this series and the alkyl nitrites, in which the rate approximately doubles for each added $-CH_2-$ group (10).

As existing theories do not take into account the quantitative details of complex dissociations, the mechanism underlying even such apparently con-sistent trends can only be guessed at.   It seems probable, however, that the observed differences in specific reaction velocities are due to differences in the proportionality factors (the A factors) of the rate expressions, so that the problem becomes one of correlating changes in A with changes in molecular structure.   It has already been suggested (2, 4) that the existence of intra-molecular "insulators" might limit the number of vibrational degrees of freedom in communication with the potentially reactive bonds, so that the rate of internal energy distribution, and hence the value of A, would depend to a certain extent on the structure of the molecule.   In the case of the ethyli-dene diacetate homologues, for example, it may be that the aldehyde radical exchanges energy with the reacting bonds more easily than do the anhydride radicals.   The fact that the effectiveness of an added $-CH_2$ - group decreases as its distance from the breaking bond increases, may mean that the latter can acquire energy from only those degrees of freedom in its immediate neighborhood.   In principle, at least, such a mechanism appears to be not unlikely.   It is indeed essentially the mechanism adopted by Hinshelwood to explain the segmented rate-pressure curves sometimes found for the low pressure decomposition of molecules of intermediate complexity (7:8, p. 215).

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

VIII. THE DECOMPOSITION OF TRICHLORETHYLIDENE DIACETATE AND TRICHLORETHYLIDENE DIBUTYRATE[1]

By N. A. D. Parlee[2], J. R. Dacey[3] and C. C. Coffin[4]

Abstract

Trichlorethylidene diacetate and trichlorethylidene dibutyrate have been found to decompose at temperatures between 200° and 290° C. at a measurable rate to give chloral and an acid anhydride. The reactions are homogeneous and of the first order, and have the same specific velocity in both the liquid and vapor states. The activation energy is identical (within experimental error) with that previously found for non-chlorinated members of this series of esters. The two compounds decompose at the same rate, in agreement with the hypothesis that the anhydride radicals do not easily exchange energy with the bonds that break. This reaction velocity, which is somewhat smaller than that of ethylidene diacetate at any temperature, is given by the equation

$$k = 1.3 \times 10^{10} \, e^{-\frac{33000}{RT}} \, .$$

Introduction

It has been shown in previous papers (for references see (3)) that the decomposition velocities of esters made from an aldehyde and an acid anhydride are sensitive to structural changes on the "aldehyde end" of the molecule. The specific reaction rate at any temperature tends to increase with the number of $-CH_2-$ groups in the aldehyde from which the ester is made. Increasing the size of the anhydride has little or no effect on the velocity of decomposition. The activation energy appears to be independent of all such structural changes. It is of interest to investigate the effect of varying the kind as well as the number of atoms in the different radicals on the activation energy and the reaction velocity.

The present paper deals with the decomposition of trichlorethylidene diacetate and trichlorethylidene dibutyrate—esters made by the addition of chloral to the respective anhydrides. These compounds have been found to behave very much like other non-chlorinated members of the series. Their decomposition is homogeneous and unimolecular, and proceeds at the same rate in both the liquid and gaseous states. They have the same decomposition velocity, which is somewhat smaller than that of ethylidene diacetate. The activation energy is the same as that of other members of the series.

Experimental

Preparation of the Esters

The esters were prepared by adding freshly distilled chloral to an equivalent quantity of the acid anhydride. A trace of sulphuric acid was used as a catalyst. After the product was washed with a solution of sodium acetate it was purified by fractional distillation *in vacuo*. A good yield of very pure

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ester is readily obtained. At atmospheric pressure the boiling points of the diacetate and the dibutyrate are about 225° and 247° C. respectively. Two independent preparations of the diacetate were used in the reaction velocity measurements.

Rate Measurements

The gas reaction was followed by the rate of pressure increase at constant volume in an apparatus of a type already described (2). Two reaction chambers (volumes, 307 and 348 cc.) were used in the experiments listed in Table I. In each case less than 1% of the total volume was below the temperature of the mercury vapor jacket. Temperatures were determined from the vapor pressure curve of mercury. The rates of decomposition were found to be independent of the partial pressure of mercury in the reaction chamber.

The velocity of the reaction in the liquid state was determined by an analytical method. Sealed tubes almost filled with an ester (0.5 to 1.0 gm.) were kept at a known temperature for a known time. The contents were then washed into water free from carbon dioxide, and, after the anhydride had changed to acid, were titrated with $0.1\,N$ barium hydroxide. The bulbs were weighed before and after emptying. Vapor thermostats at 210° (nitrobenzene) and 223° C. (methyl salicylate) were used.

Results

The data on the velocity of the gas reactions are given in Table I. The initial pressures (Column 3) are calculated by means of the ideal gas laws from the weight of ester taken. These values were always found to agree

TABLE I

REACTION VELOCITIES IN THE VAPOR PHASE

Run No.	T°, Abs.	P_o, cm. Hg.	$k \times 10^1$ (sec.$^{-1}$)	$-\log k$	$1/T$
Trichlorethylidene diacetate					
10	503.0	26.5	0.55		
11	503.0	54.7	0.60	4.268	0.001987
28	503.5	26.3	0.48		
1	513.0	28.1	1.11		
29	513.0	20.0	1.19	3.955	0.001949
2	523.0	32.4	1.64		
3	523.0	36.3	1.68		
4	523.0	33.0	1.71		
20	523.1	18.3	1.92	3.731	0.001912
21	523.0	17.4	2.09		
22	523.3	28.2	2.11		
6	533.0	28.9	3.56		
7	532.7	39.0	3.15		
8	532.9	16.0	3.46		
9	532.9	30.0	3.57		
23	533.4	17.2	3.51	3.458	0.001874
24	533.0	31.7	3.11		
25	533.2	22.5	3.76		
26	532.8	20.3	3.76		

TABLE I—*Concluded*

REACTION VELOCITIES IN THE VAPOR PHASE—*Concluded*

Run No.	T°, Abs.	P_o, cm. Hg.	$k \times 10^4$ (sec.$^{-1}$)	$-\log k$	$1/T$
Trichlorethylidene diacetate—Concluded					
12	542.0	22.0	6.37		
13	543.0	27.3	6.55	3.188	0.001841
27	543.0	21.8	6.53		
30	543.0	23.7	6.45		
14	553.0	36.2	12.3		
15	553.0	24.0	12.4	2.909	0.001808
16	553.0	16.0	12.3		
17	553.0	5.0			
31	563.0	26.8	21.3	2.680	0.001776
32	562.9	8.9	20.5		
Trichlorethylidene dibutyrate					
13	514.1	5.3	1.2	3.839	0.001947
20	513.0	21.3	1.7		
11	522.7	7.8	1.97	3.688	0.001912
12	523.2	11.5	2.14		
7	533.0	14.4	4.43		
8	532.9	12.7	4.51	3.369	0.001876
15	533.2	11.4	3.9		
5	543.1	15.1	8.58		
6	542.9	15.4	8.15		
9	543.0	14.3	8.28	3.058	0.001842
16	543.1	9.3	10.0		
21	543.0	25.3	8.7		
3	552.9	21.6	13.2		
4	553.0	15.6	14.0		
19	552.9	22.1	15.1	2.854	0.001808
22	553.0	21.2	13.7		
1	563.1	18.8	23.1		
10	562.9	20.4	26.9	2.613	0.001776
18	562.9	24.2	23.1		

within several millimetres with that obtained by extrapolating the observed pressures (corrected for the partial pressure of mercury vapor and the difference in temperature of the two sides of the manometer) to zero time. Within the limits of error of the extrapolation, the initial pressure was always found to be one-half the final pressure in spite of the fact that a secondary reaction caused a slow but steady drift in the latter. This increase, which amounts to 2 or 3% in 24 hr. at any temperature, is easily corrected for. It is probably due to a heterogeneous polymerization and decomposition of chloral on the chamber walls, which become more and more thickly coated with a brown lacquer-like film.

The majority of the first order velocity constants listed in Column 4 were calculated by the Guggenheim method (4). In cases where it was not convenient to take readings at equal time intervals, $\log \dfrac{P_o}{2P_o - P}$ was plotted against time, and the velocity constant was obtained from the slope of the resulting straight line. The agreement between the two methods was in general very satisfactory. The data of a typical run (trichlorethylidene diacetate, No. 16) worked up by both methods are plotted in Fig. 1. It is evident that the reaction is strictly first order, and that no appreciable error is introduced by the uncertainty in the initial and final pressures.
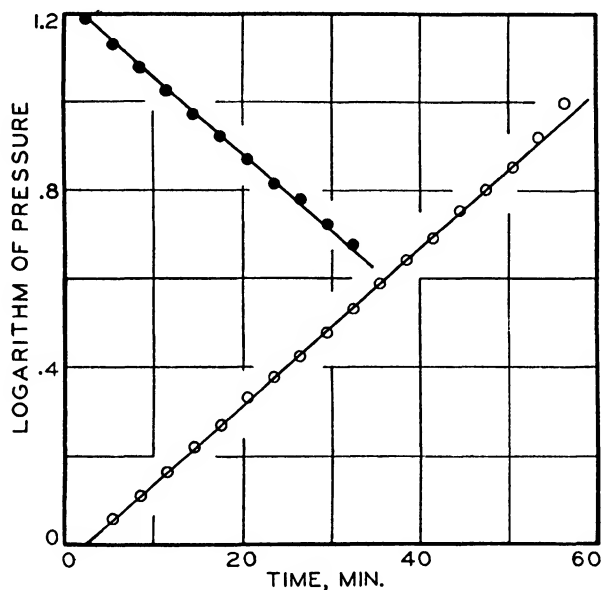
FIG. 1. Data of a typical run. ●, Guggenheim method; ○, $\log \dfrac{P_o}{2P_o - P}$.

The values obtained for the reaction rates in the liquid state are summarized in Table II. The percentage reaction given in Column 4 is the mean of two determinations carried through in duplicate. These usually agreed within about 2%. The contents of the bulbs gradually became dark red at the reaction temperature. If left in the thermostat for a long time (decomposition = 80–90%), the reaction mixture became badly charred, and a high pressure of permanent gas developed. This secondary reaction is believed to be the decomposition of chloral or of one of its polymers, as it does not occur in the case of some esters made from the same anhydrides and other aldehydes.

The quite satisfactory agreement between the first order velocity constants (uncorrected for any reverse reaction) found for different reaction times indicates that the decomposition in the liquid state is unimolecular and that it goes to completion. This reaction in the pure liquid state and in solution is being more fully investigated.

TABLE II

DECOMPOSITION IN THE LIQUID STATE

Bulb No.	Temp., °Abs.	Time, hr.	Reaction, %	$k \times 10^5$	$-\log k$ (mean)	$1/T$ (mean)
Trichlorethylidene diacetate						
1, 2	483.2	4.6	25.3	1.77		
3, 4	483.6	2.0	11.2	1.79		
5, 6	483.6	5.0	26.4	1.70	4.765	0.002068
7, 8	483.6	16.0*		1.63		
9, 10	483.6	2.8	15.3			
11, 12	496.4	4.0	58.5	6.1		
13, 14	496.3	1.0	15.8	4.8		
15, 16	496.3	2.5	36.2	5.0	4.339	0.002010
17, 18	496.3	5.0*	89.7	5.2		
19, 20	496.3	1.5	24.4			
Trichlorethylidene dibutyrate						
1, 2	483.4	4.0	20.0	1.55		
3, 4	483.1	5.0	23.7	1.51	4.815	0.002070
5, 6	482.9	7.2	32.8	1.54		
7, 8	495.5	1.0	17.4	5.3		
9 10	495.4	2.0	24.2	3.8	4.347	0.002018

* *Charred.*

The mean negative logarithms of the velocity constants and the mean reciprocal temperatures (Columns 5 and 6, Table I; 6 and 7, Table II) are plotted against each other in Fig. 2.

It is evident from Fig. 2 that the two compounds decompose at practically the same rate at all temperatures and that this is the same in both the liquid and gaseous states. It is true that on the average the dibutyrate
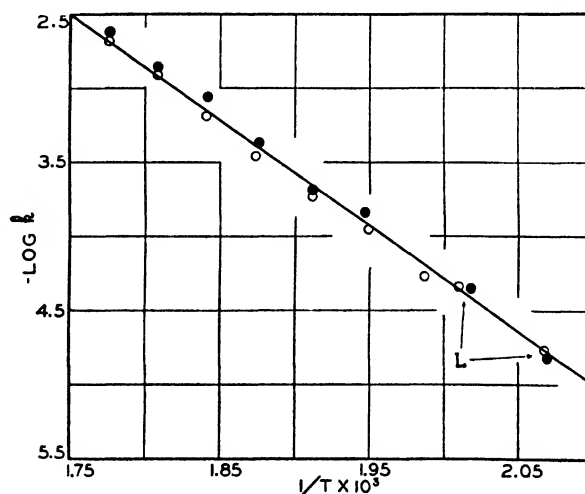
FIG. 2. —*Log k plotted against 1/T.* ○, *Trichlorethylidene diacetate;* ●, *trichlorethylidene dibutyrate; L, indicates experiments in liquid state.*

points appear to be slightly higher than those of the diacetate. However, as the difference is probably within the limit of error of the present experiments, the two compounds may be tentatively regarded as decomposing at the same rate. This rate at any temperature is given by the equation (that of the straight line in Fig. 2)

$$k = 1.3 \times 10^{10} e^{-\frac{33000}{RT}}.$$

The decomposition velocity of ethylidene diacetate is given by the equation $k = 2.0 \times 10^{10} e^{-\frac{33000}{RT}}$. It is evident that within the accuracy of the data the trichlor-esters have the same activation energy as the other members of the series.

The fact that the activation energy is unchanged and that the A factor (*cf.* the equation $k = A e^{-\frac{E}{RT}}$) is changed only slightly by the substitution of three chlorine for three hydrogen atoms, is of considerable interest. It is remarkable that the stability of a bond (as measured by the energy necessary to break it) should be unaffected by weighting a neighboring atom so heavily. One might also expect that the specific reaction rate would undergo a greater change, particularly since the substitution is made in the only radical whose structure has been found to influence the rate (3). Other substitutions and structures are being investigated.

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STUDIES ON HOMOGENEOUS FIRST ORDER GAS REACTIONS

IX. THE DECOMPOSITION OF FURFURYLIDENE DIACETATE AND CROTONYLIDENE DIACETATE[1]

By J. R. Dacey[2] and C. C. Coffin[3]

Abstract

The vapor phase decomposition of furfurylidene diacetate and crotonylidene diacetate to acetic anhydride and their respective aldehydes is homogeneous, first order, and complete. The activation energy is that characteristic of the series, *viz.*, 33,000 cal. The specific reaction rates of the two esters are the same, and are about six times as great as that of ethylidene diacetate at any temperature. It is suggested that the increased velocity is due to the presence of the double bond. Velocity constants are given by the equation

$$k = 1.3 \times 10^{11} \, e^{-\frac{33000}{RT}}.$$

Introduction

Previous papers of this series (3) have shown that the addition of $-CH_2-$ groups or chlorine atoms to ethylidene diacetate has little or no effect on the amount of energy required before the ester molecule decomposes into an aldehyde and an anhydride; that the influence of such structural alterations on the velocity of decomposition is not very large, and that it is apparently confined to the aldehyde end of the molecule. It is of interest to study the effect of more complex structural changes on the activation energy and reaction velocity.

The present paper deals with the breakup of furfurylidene diacetate and crotonylidene diacetate to acetic anhydride plus furfural and crotonaldehyde respectively. The former ester is characterized by a furan ring, the latter by a straight chain. Each has a double bond at the same distance from the point at which the molecules break. As is the case with other members of the series the vapor phase decomposition is homogeneous, unimolecular, and complete. Within experimental error the activation energy of each compound is that characteristic of the series. Their specific reaction velocities are identical, and are about six times as great as that of ethylidene diacetate and four times as great as that of butylidene diacetate at any temperature. It thus appears that the furan ring has no effect on the rate of the reaction or the stability of the molecule, and that the double bond is responsible for the observed velocity increase.

Experimental

The esters were prepared by refluxing the freshly distilled aldehydes with acetic anhydride containing a trace of sulphuric acid. They were purified and analyzed by methods already described (1, 3).

The reaction rate measurements were made in an improved apparatus (4). Velocity constants were calculated from the rate of pressure increase in the usual manner.

Results

The data are presented in Table I, which is self-explanatory.

TABLE I

SUMMARY OF REACTION VELOCITY DATA

Run No.	Temp., °Abs.	P_o, cm. Hg.	$k \times 10^3$, (sec.$^{-1}$)	$-\log k$	$1/T \times 10^3$
Furfurylidene diacetate					
21	493.1	18.8	0.326	3.507	2.028
22	493.1	33.6	0.297		
10	503.3	13.8	0.599	3.214	1.988
11	503.1	19.1	0.653		
12	503.1	2.0	0.650		
17	502.9	17.5	0.541		
6	513.1	18.1	1.14	2.963	1.949
8	513.1	12.2	1.15		
9	513.1	24.5	0.99		
1	523.0	52.1	2.03	2.701	1.912
2	523.0	39.9	2.01		
3	523.1	23.9	1.85		
4	522.9	10.4	2.04		
5	522.9	18.3	2.04		
13	532.7	16.2	3.03	2.434	1.877
15	532.8	33.0	4.05		
16	532.8	26.0	3.95		
18	542.9	17.5	7.26	2.148	1.842
19	542.9	41.6	6.85		
20	542.9	15.9	7.23		
23	553.0	23.0	13.4	1.917	1.808
25	552.9	19.1	11.3		
26	553.0		12.2		
27	553.0		12.3		
28	553.0	29.0	10.7		
29	553.0	7.2	13.0		
Crotonylidene diacetate					
4	492.0	42.1	0.379	3.456	2.032
5	492.1	12.3	0.331		
6	492.2	13.5	0.343		
7	503.7	34.1	0.615	3.199	1.986
8	503.5	19.7	0.655		
9	503.5	16.9	0.628		
1	513.0	26.4	0.97	2.943	1.952
10	511.9	30.7	1.32		

TABLE I.—*Continued*

SUMMARY OF REACTION VELOCITY DATA—*Continued*

Run No.	Temp., °Abs.	P_o, cm. Hg.	$k \times 10^3$, (sec.$^{-1}$)	$-\log k$	$1/T \times 10^3$
Crotonylidene diacetate—Concluded					
23	515.0	17.8	1.1 ⎫		
24	515.0	7.1	1.2 ⎬ 2.920	2.920	1.942
25	515.0	4.4	1.4		
26	515.0	11.7	1.2 ⎭		
11	522.6	21.2	2.23 ⎫		
12	522.2	26.9	2.29 ⎬	2.631	1.914
13	522.4	19.7	2.51 ⎭		
14	533.3	24.6	4.04 ⎫		
15	533.1	51.3	3.52 ⎬	2.411	1.875
16	533.4	9.6	4.08 ⎭		
22	539.0	27.7	4.8	2.32	1.855
17	543.2	19.5	7.10 ⎫		
18	543.2	23.5	6.33 ⎬	2.167	1.841
19	543.2	10.6	6.99 ⎭		
20	533.2	7.7	13.8 ⎫		
21	533.2	18.7	12.0 ⎬	1.900	1.808
2	533.0	18.1	12.1 ⎭		

In Fig. 1 the negative logarithms of the velocity constants (Column 5) are plotted against the reciprocals of the absolute temperatures. In order to conform with the previously adopted assumption (1, 2) that velocity differences are due to variations in the A factor of the rate equation, the
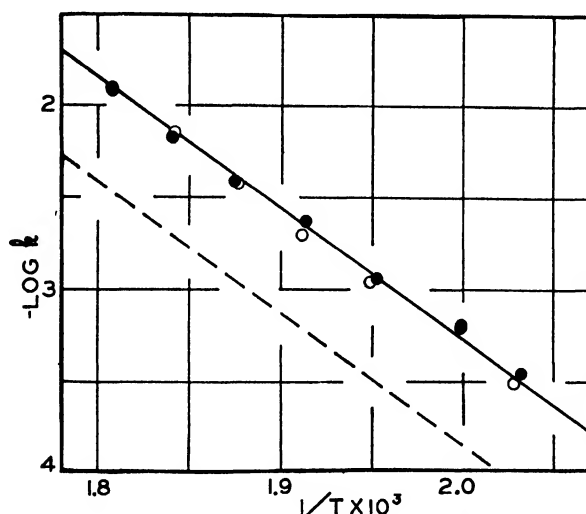
FIG. 1.   —*Log k plotted against* 1/*T.   Broken line, butylidene diacetate;* O,
furfurylidene diacetate; ●, *crotonylidene diacetate.*

straight line of Fig. 1 has been arbitrarily given a slope corresponding to an activation energy of 33,000 cal. It is obvious that the line fits the data within experimental error. For purposes of comparison the position of the butylidene diacetate line is indicated on the diagram. Velocity constants of the furfurylidene and crotonylidene diacetate decomposition are given by the equation $k = 1.3 \times 10^{11} e^{-\frac{33000}{RT}}$.

A comparison of the reaction rates and structural formulas of butylidene and crotonylidene diacetates at once suggests that the enhanced reactivity of the latter is due to the presence of the double bond. Moreover, unless the correspondence between the crotonylidene and furfurylidene velocities is entirely fortuitous, it would seem that the double bond is the only difference (as far as factors influencing reaction rate are concerned) between the butylidene and furfurylidene esters. Further discussion is reserved until more data have been collected.

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THE REACTION OF DEUTERIUM ATOMS WITH METHANE AT HIGH TEMPERATURES[1]

By E. W. R. Steacie[2]

Abstract

Using the Wood-Bonhoeffer method, an investigation has been made of the reaction of deuterium atoms with methane at temperatures up to 500° C. Owing to the difficulties involved in poisoning the walls to prevent atom recombination at high temperatures, the atom concentration was very variable. The results are therefore only approximate, but they serve to establish definitely the presence of a reaction at the temperatures under investigation, and enable the estimation of the activation energy of the reaction

$$D + CH_4 = CH_3D + H_2,$$
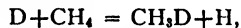
viz., 12.9 ±2 Kcal. This is in good agreement with values obtained in other investigations.

Introduction

In the past few years the kinetics of a number of reactions involving atomic deuterium has been investigated.* Investigations of this kind often permit conclusions to be drawn regarding the rates of other atomic processes, and such information is of great interest, especially in connection with recent speculations regarding the participation of free radicals in chemical processes.

The reactions of hydrogen and deuterium atoms with methane have been the subject of considerable investigation. Early experiments (1, 16) showed that methane was unique in that it alone of the hydrocarbons seemed to be without effect on atomic hydrogen, being unattacked by it, and causing no "catalysis" of the recombination of hydrogen atoms. Ethane catalyzes the recombination of hydrogen atoms but is not appreciably attacked, while all other hydrocarbons react readily. Geib and Harteck (7) confirmed the above results and showed that no reaction occurred up to 183° C. They therefore concluded that the reaction $CH_4 + H = CH_3 + H_2$ has an activation energy of at least 17 Kcal.

Taylor, Morikawa, and Benedict (14) investigated the reaction of methane with deuterium atoms produced by photosensitization with mercury. The resulting deuteromethanes were detected by infra-red spectroscopy. They reported considerable reaction from 40° to 300° C., and concluded that the activation energy of the process was very low, of the order of 5 Kcal. They assumed that the primary reaction was $CH_4 + D = CH_3 + HD$.

Geib and Steacie (8, 9) investigated the same reaction by the Wood-Bonhoeffer method. They found no detectable reaction of deuterium atoms with methane up to 100° C. This indicated that the activation energy of the exchange reaction is equal to or greater than 11 Kcal., in sharp contrast to the result of Taylor, Morikawa, and Benedict. Their investigation

indicated (by analogy with the reaction of deuterium atoms with other substances) that the reaction concerned is probably the analogue of the ortho-para hydrogen conversion, *viz.*

$$CH_4 + D = CH_3D + H,$$

rather than

$$CH_4 + D = CH_3 + HD.$$
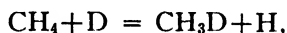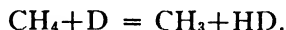
In any case, the investigation sets a lower limit of 11 Kcal. for the activation energies of both reactions.

Farkas (3) made a few preliminary experiments on the thermal exchange reaction between deuterium and methane at temperatures in the neighborhood of 1000° K. He showed that the thermal reaction proceeds by an atomic mechanism similar to that of the ortho-para hydrogen conversion, *viz.*

$$D_2 = 2D$$
$$D + CH_4 = CH_3D + H. \tag{1}$$
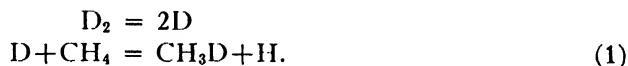
His results indicate that the activation energy is in the neighborhood of 11 Kcal.

The mercury photosensitized reaction was reinvestigated by Steacie and Phillips (13). In agreement with the results of Farkas and of Geib and Steacie they found an activation energy of about 11.7 Kcal. for the exchange reaction. The reaction was also investigated by Farkas and Melville (5) over a wide range of temperature, and they found an activation energy of 13 Kcal. They concluded, as did Steacie and Phillips, that the reaction was the analogue of the ortho-para hydrogen conversion. They found, however, that at high temperatures the D-atom concentration fell off greatly, and they suggest that the atom-consuming step is the reaction

$$D + CH_4 = CH_3 + HD. \tag{2}$$

On this basis we would expect a small amount of ethane formation to accompany the exchange reaction.

Since the submission of the present paper, a report of a further investigation of the mercury photosensitized reaction by Morikawa, Benedict, and Taylor (12) has appeared. From the collision yield at 100° C. they calculate an activation energy of 12.5 to 14 Kcal. for Reaction (1) in good agreement with Steacie and Phillips and with Farkas and Melville. The experimental value of the temperature coefficient is very low, however, and they conclude that the true mechanism is not that indicated by Reaction (1). They suggest that the reaction is largely

$$Hg^* + CH_4 = CH_3 + H + Hg$$
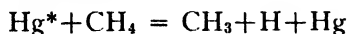
followed by a rapid exchange of the methyl radical probably through the formation and decomposition of a quasi-molecule CH_3D^*. The fact that some ethane formation occurs is cited as evidence for the presence of methyl radicals. They discuss a large number of possible secondary reactions, and conclude that one cannot obtain much information about Reaction (1) by the photosensitization method.

It seems to the writer, however, that the loss of hydrogen atoms at high temperatures found by Farkas and Melville is a sufficient explanation of the low temperature coefficient of the reaction, and that the postulation of a complicated series of processes is unnecessary. It should be noted that the experimental results of Morikawa, Benedict, and Taylor are in good agreement with those of previous investigations, the discrepancy being primarily one of interpretation.

In a further paper Trenner, Morikawa, and Taylor (15) report an investigation by the Wood-Bonhoeffer method. They found no reaction from 25 to 208° C., from which they calculate a minimum activation energy of 15.6 Kcal, for the exchange reaction. From a single run at 310° C. they calculate the activation energy to be 18 Kcal. These values are considerably higher than those obtained by other workers. The discrepancy is partly due to the fact that they assume that the primary reaction is No. 2, followed by a rapid exchange of the methyl radical. Hence to get the rate of the first step they divide the observed rate by 3. If the primary reaction is really No. 1 as concluded by all other workers in the field, this division should not be performed, and their activation energy will be lowered by nearly 1 Kcal.

All these investigations of the deuterium atom reaction prove conclusively that the activation energy of the reaction $CH_4 + H = CH_3 + H_2$ must be about 12 to 13 Kcal. In his recent review Geib points out that further evidence of the stability of methane to attack by hydrogen atoms is indicated by the fact that methane is obtained as an end product in many H-atom reactions.

It appears, therefore, that the results obtained by photosensitization, thermal, and discharge tube methods present a consistent picture. It would, however, be highly advantageous to have the H-atom results at low temperatures extended so as to approach the high temperature thermal range, and thus complete the investigation of the whole scheme. This has been attempted in the present investigation. Although, owing to experimental difficulties, the results are only approximate, nevertheless they do serve to establish fairly definitely the activation energy of the reaction by the discharge tube method, and to show that the results of all methods of investigation are entirely consistent.

Experimental

For the reasons outlined above, and also for the investigation of other reactions, it would be very desirable to be able to extend the Wood-Bonhoeffer method to high temperatures. Apparently no previous attempt to do this has been made. The main difficulty in doing so is, of course, obvious. The successful operation of the method requires the prevention of too fast a recombination of hydrogen atoms on the walls of the apparatus. This can be done only by poisoning the walls, and such poisoning has been previously accomplished by running the tube wet, or by coating the walls with phosphoric acid, potassium chloride, or sulphuric acid. At high temperatures the use of a wet tube, or of sulphuric acid, is impossible.

In preliminary experiments a quartz reaction vessel was used, and attempts were made to poison it with phosphoric acid and with potassium chloride. It was found that, apart from any question of the efficacy of poisoning agents, quartz is not a suitable material. In the process of blowing the quartz apparatus a certain amount of devitrification is almost inevitable, and it was found to be virtually impossible to poison such devitrified spots even at temperatures of 100° to 200° C.

The apparatus was therefore rebuilt of Pyrex glass. With this apparatus it was found that potassium chloride was definitely unsuitable for poisoning purposes at high temperatures. Attempts to run the apparatus with a very thoroughly cleaned wall without poisoning were unsuccessful, as might have been expected. A wall coated with phosphoric acid was satisfactory up to about 300° C. Above this temperature the phosphoric acid first dehydrated, and finally the dry phosphorus pentoxide largely distilled out of the reaction vessel. By coating fairly heavily, heating to high temperatures for the minimum possible time, and using "wet" hydrogen, it was possible to obtain a fair amount of success with phosphoric acid up to 500° C.

To get the maximum possible atom concentration at high temperatures, the reaction vessel was moved as close as possible to the discharge (about 5 cm.), and the partial pressure of methane was made very low to prevent its blowing back into the discharge. A small amount of methane did nevertheless get into the discharge, and this raised the "blank" correction by 3% or so, but this was unavoidable.

Under these conditions it was possible to obtain high atom concentrations and reasonably reproducible results up to about 350° C. At 500° C. the atom concentration was still appreciable (about 2%), but was very variable (by a factor of 2 or 3). However, it was possible nevertheless to make approximate measurements up to this temperature.

Apparatus

The main section of the apparatus is shown in Fig. 1. A discharge was run through the tube *A* (1 in.
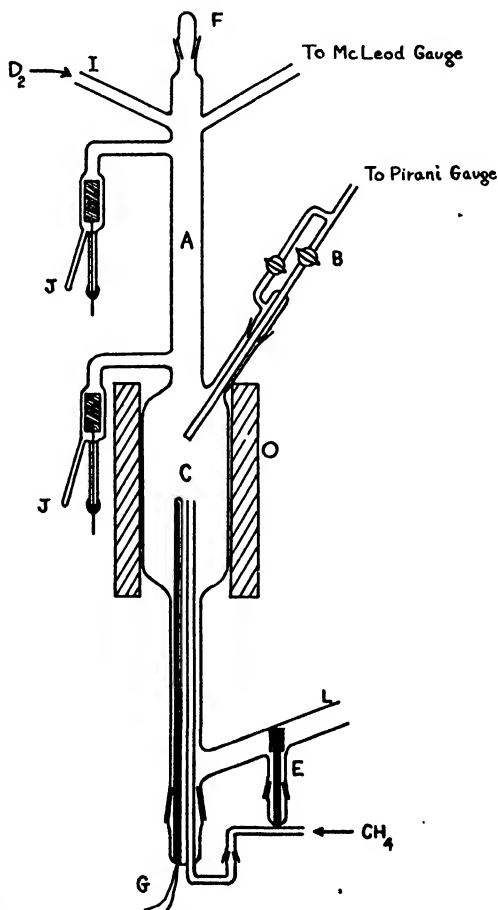
FIG. 1. *Apparatus.*

diameter).   The electrodes were aluminium cylinders attached to stout platinum leads which were taken out through a capillary tube sealed with deKhotinsky cement.   The discharge was operated with an applied voltage of about 3500 across the tube and a 5000 ohm resistance.   The voltage was varied with a step transformer and a rheostat in the primary so as to maintain a constant current of 340 milliamperes through the tube.

Below the discharge was a reaction vessel C, with a diameter of 7 cm. and a length of 40 cm.   This was surrounded by an electric furnace O, which could be slipped up and down the tube so as to permit observation when the efficiency of the wall poisoning, etc., was tested.   Two tubes entered the reaction vessel from below, one of which contained a thermocouple, and the other served as an inlet for methane.

The hydrogen atom concentration in the reaction vessel was measured with the Wrede gauge B.   This was of the usual type (10, 17) and consisted of a tube B with a very fine orifice situated in the reaction vessel, and an arrangement of stopcocks such that either the inside of the tube or the outside could be connected to a Pirani gauge.   On account of the difference in the diffusion coefficients of hydrogen atoms and hydrogen molecules, a pressure difference will be set up across the orifice, and this may be measured with the Pirani gauge.   From the pressure difference the percentage of atoms in the vessel may be readily calculated.   In addition, to serve as a rough check on the efficacy of the poisoning, etc., an ordinary mercury thermometer was placed at E with its bulb wrapped with platinum gauze and situated in the gas stream.   A heating up to 50 or 60° C. could be obtained, and this gave a very rough measure of the atom concentration of the gas leaving the reaction vessel.

To facilitate poisoning the walls of the apparatus, the whole main section was made vertical as indicated.   In order to wash the apparatus the ground cap F at the top, the inlet tubes and joint G, and the Wrede gauge B were removed.   The tips were then cut off the small drainage tubes, J, attached to the electrodes.   The apparatus was then washed out with distilled water, fuming nitric acid, water again, and finally with a 5% solution of phosphoric acid.   The ground joints were then replaced, the tips of the tubes J sealed off, and the apparatus was dried by evacuation.

Deuterium was prepared in part by the electrolysis of alkaline 99.6% deuterium oxide, and in part by the reaction of 99.6% deuterium oxide with sodium.   It was stored in a large bulb, and was pumped as required into a small mercury gas-holder by means of a Toepler pump.   It then passed through a bubbler containing deuterium oxide, and a capillary flowmeter, and entered the apparatus at I.   The flowmeter was adjusted so as to maintain the pressure in the apparatus at 0.30 mm.

Methane was secured in cylinders from the Ohio Chemical and Manufacturing Co. and was stated to be 96.5% methane.   It was purified by fractional distillation and stored in a large reservoir.   In making an experiment it was expanded into a small reservoir connected to the apparatus through a flowmeter.   By adjusting the pressure in the small reservoir it was possible to secure any desired rate of flow.

After leaving the reaction vessel through the outlet tube L, the gas passed through a trap at liquid air temperature and a three stage steel mercury diffusion pump. This had a very high speed (approximately 20 litres per sec.) and could maintain a pressure of 0.30 mm. in the apparatus when deuterium was admitted at the rate of about 13 cc. at N.T.P. per minute. After leaving the diffusion pump the gas passed through a trap containing silica gel at $-180°$ C. to remove the methane, and then to a Hyvac pump.

At the end of an experiment, which normally lasted about 15 min., the silica gel trap was maintained at $-180°$ C. and pumped out for 5 min. with the Hyvac pump alone. Trials showed that it was possible to desorb virtually all adsorbed hydrogen in this way without appreciable loss of methane. The trap was then allowed to warm up to $0°$ C. to desorb the methane. The methane was then expanded into a two litre combustion pipette, dry oxygen was admitted, and the methane was burned on a platinum filament. The resulting water was freed from oxygen and carbon dioxide by repeated distillations at $-80°$ C. in a high vacuum. The water was then analyzed for its deuterium content by the thermal conductivity method of Harteck as described in previous papers.

Experimental Results

Atom Concentration

As was mentioned above, the deuterium atom concentration was measured with a Wrede diffusion gauge. In order to conserve deuterium, the atom concentration measurements were made in special calibration experiments using ordinary hydrogen. This introduces no appreciable error for the following reasons. If the pressure is kept the same, hydrogen will flow through the apparatus faster than deuterium and will take less time to get from the discharge to the reaction vessel. During this time, however, it will undergo more collisions on account of its higher molecular velocity. These two effects balance, and there will be no appreciable difference in the number of collisions undergone by hydrogen or by deuterium atoms (or molecules) while traveling between the discharge tube and the reaction vessel. Also, the activation energies of the recombination reactions

$$H+H(+M) = H_2(+M)$$

and

$$D+D(+M) = D_2(+M)$$
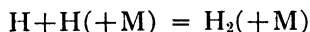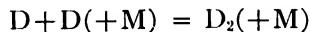
will not differ appreciably since atoms have no zero-point energy. Hence, we may expect the same atom concentration in the reaction vessel irrespective of whether hydrogen or deuterium is used. In any case, any possible error from this source is negligible compared to the uncertainties in the atom concentration on account of fluctuations in the activity of the walls.

At low temperatures the results were definitely reproducible and indicated an average of 36% atoms at $20°$ C. and 20% at $250°$ C. At $350°$ C. an average of about 10% was obtained, but the activity of the walls fluctuated consider-

ably and this value is probably good only to within a factor of 1.5 to 2.   At 450° to 500° C. the variations were still more pronounced.   The atom concentration was about 2%, but this value is probably uncertain by a factor of 3, and perhaps 4.

Blank Experiments

On account of the small distance between the reaction vessel and the discharge, a very small, but definite amount of methane diffused back into the discharge against the deuterium flow.   Inasmuch as a number of previous investigations, and preliminary results in the present work, had all shown that methane is not attacked by deuterium atoms at 20° C., it was possible to use runs at this temperature as blanks to estimate the effect of the penetration of methane into the discharge.

Six experiments of this type under conditions similar to those in the experiments reported indicated that the products of the reaction at 20° C. were 3.0, 4.9, 4.5, 4.7, 5.6, and 4.3% "heavy". The mean, 4.5%, was therefore used as a correction for this factor, and was subtracted from the percentage conversion of CH_4 to CD_4 obtained in the high temperature experiments. This blank value is rather high, but in order to have reduced it, it would have been necessary to increase the D_2/CH_4 ratio to such an extent that very long times, and therefore very large amounts of deuterium, would have been necessary in order to obtain sufficient methane for analysis. (As it was, about 220 cc. of deuterium at N.T.P. were consumed in each experiment.) Actually, however, the blank experiments were very reproducible, and no more uncertainty arises from this cause than is inevitably present on account of the fluctuations in the deuterium atom concentration at high temperatures.

Results

The results of all runs made with the apparatus in its final form are given in Table I.

In arriving at the values tabulated, knowing the rate of flow of deuterium and methane, we first calculate the total volume of gas flowing per second at the temperature and pressure of the reaction vessel. From this and the volume of the reaction vessel we arrive at the reaction time.   In performing the calculation it is necessary to correct the gas volume for the expansion due to the splitting of part of the deuterium into atoms.

From a knowledge of the fraction of deuterium present as atoms, and the total pressure, we then get the partial pressure of deuterium atoms in the system and the number of deuterium atoms per cubic centimetre in the reaction vessel.   We then calculate $Z_{CH_4,D}$, the number of collisions made by one methane molecule with deuterium atoms in one second.   This is obtained from the relation*

$$Z_{CH_4,D} = 2\sqrt{2\pi}\left(\frac{d_D + d_{CH_4}}{2}\right)^2 \sqrt{\frac{M_D + M_{CH_4}}{M_D M_{CH_4}}} \cdot RT \times N_D ,$$

* See K. F. Herzfeld (11, p. 46) or Bonhoeffer and Harteck (2, p. 183).

TABLE I

THE REACTION OF DEUTERIUM ATOMS WITH METHANE

Temperature, °C.	Atoms, %	Total flow of gas in cc. per sec. at the temp. and press. of the expt.	Total volume corrected for amount of D_2 present as atoms	Time in reaction vessel, sec.	Partial pressure of D atoms, cm.	N_D, the number of D atoms per cc.	Z_{CH_4}, D per sec.	Z_{CH_4}, D in reaction time	CD_3 in products, (uncorrected), %	CD_3 (corrected), %	Exchange, %	Collision yield	E, Kcal, assuming A = 0.1	E, Kcal, assuming A = 0.01
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{13}	5.34×10^{5}	6.35×10^{5}	7.0	2.5	2.8	1.8×10^{-7}	13.7	11.3
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{13}	5.34×10^{5}	6.35×10^{5}	7.4	2.9	3.3	2.0×10^{-7}	13.6	11.2
250	20	1043	1153	1.19	5.6×10^{-3}	1.04×10^{13}	5.34×10^{5}	6.35×10^{5}	6.4	1.9	2.1	1.4×10^{-7}	14.0	11.6
350	10	1243	1308	1.05	2.8×10^{-3}	4.40×10^{11}	2.48×10^{5}	2.61×10^{5}	9.5	5.0	5.6	8.7×10^{-7}	14.4	11.5
350	10	1243	1308	1.05	2.8×10^{-3}	4.40×10^{11}	2.48×10^{5}	2.61×10^{5}	11.3	6.8	7.7	1.2×10^{-6}	14.0	11.2
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{10}	4.55×10^{4}	4.27×10^{4}	14.3	9.8	11.0	1.0×10^{-5}	13.1	9.8
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{10}	4.55×10^{4}	4.27×10^{4}	10.6	6.1	6.9	6.4×10^{-6}	13.8	10.5
450	2	1442	1456	0.94	5.6×10^{-4}	7.53×10^{10}	4.55×10^{4}	4.27×10^{4}	14.7	10.2	11.5	1.1×10^{-5}	13.1	9.8
500	2	1542	1557	0.88	5.6×10^{-4}	7.04×10^{10}	4.41×10^{4}	3.88×10^{4}	11.1	6.6	7.5	7.7×10^{-6}	14.4	11.0
500	2	1542	1557	0.88	5.6×10^{-4}	7.04×10^{10}	4.41×10^{4}	3.88×10^{4}	10.4	5.9	6.7	5.9×10^{-6}	14.8	11.3

Volume of reaction vessel = 1370 cc.; deuterium flow = 0.202 cc. per sec. at N.T.P.; methane flow = 0.0130 cc. per sec. at N.T.P.; pressure = 0.30 mm.

where the d's are the molecular diameters and the M's the molecular weights. Assuming the diameter of the methane molecule to be 3.0×10^{-8} cm., and the collision diameter of a deuterium atom to be the same as that of a hydrogen atom (10), this reduces to

$$Z_{CH_4.D} = 2.25 \times 10^{-11} N_D\sqrt{T},$$

whence we get the values given in Column 8. We then get the number of collisions occurring during the reaction time. The next two columns give the percentage conversion to CD_4, before and after correcting for the blank experiments. From this we get the "percentage exchange" on the assumption that complete exchange would correspond to a uniform distribution of deuterium and hydrogen between methane and hydrogen. The collision yield is then calculated, it being remembered that it takes four fruitful collisions to convert a molecule of CH_4 to CD_4. The back reaction $CD_4+H = CD_3H+D$ has been neglected, since its effect is insignificant for small percentage conversions. The last two columns give the activation energy calculated from the collision yield according to the relation

$$\text{collision yield} = Ae^{-E/RT},$$

the value of E being calculated on the assumption that the steric factor is 0.1 in one case and 0.01 in the other.

Discussion

In Fig. 2 the logarithm of the collision yield is plotted against $1/T$. The activation energy calculated from the slope of the full line is 13.5 Kcal. The two dotted lines correspond to 11.5 and 15.3 Kcal. respectively. It is apparent that all that can be said from a consideration of the temperature coefficient is that E is 13.5 ± 2 Kcal.
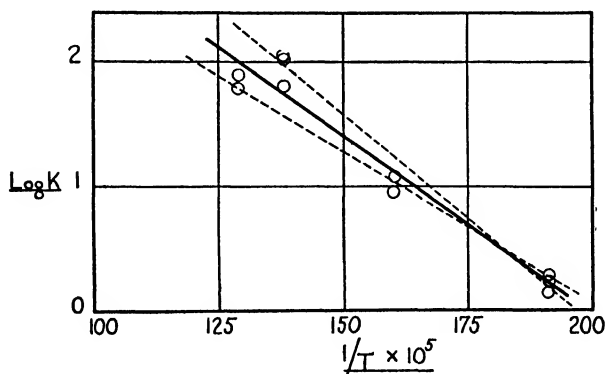
FIG. 2. *The temperature coefficient of the collision yield.*

In Table I the calculated activation energies for each run are shown, the values having been obtained by assuming steric factors of 0.1 and 0.01. The corresponding mean values of E are 13.9 and 10.9 Kcal. respectively. The reaction apparently proceeds in a manner analogous to the reaction

$H_2+D_2 = 2HD$, for which the steric factor is 0.07 (4). Farkas (3) has pointed out that there are grounds for believing that the steric factor in the reaction $D+NH_3$ is only one-quarter as great as this. The methane molecule is more symmetrical than the ammonia molecule, and perhaps the most plausible value for the steric factor is about 0.04. If we assume this we get for E about 12.9 Kcal., which is in complete agreement with that calculated from the temperature coefficient. On account of the fluctuations in the atom concentration and of the relatively large "blanks", the results are only approximate. Making a rather liberal estimate of the probable error, we may state the activation energy to be 12.9 $\pm$ 2 Kcal. This is in good agreement with previous estimates, *viz.*

Geib and Steacie (Wood-Bonhoeffer method at low temperatures)	>11 Kcal.
Steacie and Phillips (mercury photosensitization)	11.7
Farkas (Thermal. E not determined but by analogy with the $D+NH_3$ reaction may be estimated as roughly)	11
Farkas and Melville (mercury photosensitization)	13
Morikawa, Benedict, and Taylor (mercury photosensitization)	12.5 to 14
Trenner, Morikawa, and Taylor (Wood-Bonhoeffer method up to 300° C.)	15.6

The results of the present investigation, therefore, although they are only approximate, serve to tie-in the low temperature atomic technique and the high temperature thermal results. The activation energy of the reaction would certainly seem to be established as not far from 12 to 13 Kcal.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XV. DICENTRA CHRYSANTHA WALP. AND DICENTRA OCHROLEUCA ENGELM[1]

By Richard H. F. Manske[2]

Abstract

Bicuculline, protopine, and cryptopine have been isolated from both of the species mentioned in the title. In addition, *Dicentra chrysantha* was found to contain two new alkaloids, namely, $-\nu$, $C_{19}H_{17}O_6N$, phenolic, and *chrycentrine*, $C_{18}H_{15}O_5N$, non-phenolic. Neither alkaloid contains methoxyl groups. A very small quantity of a sixth alkaloid, as yet not characterized from *D. chrysantha*, proved to be identical with a base recently isolated from *Corydalis ochotensis*.

Dicentra chrysantha Walp. and *D. ochroleuca* Engelm. are closely related species native to California. In the genus *Dicentra* they are exceptional because of their remarkable upright caulescent habit. Of the species that have been chemically examined only the Asiatic *D. spectabilis* has a stem. All others are stemless and this distinctive habit is reflected not only in the large number of contained alkaloids but in their character. *D. cucullaria* is the only species of the stemless group that thus far has not yielded an alkaloid of the aporphine type.

Owing to the relative inaccessibility of the plants under discussion, it has not been possible to carry their investigation as far as is desirable. In view of the fact, however, that more material will not be immediately available, it seemed expedient to publish the present observations.

Six alkaloids have been isolated from *D. chrysantha* and of these, bicuculline, protopine, and cryptopine are already known. A fourth alkaloid proved to be identical with one recently isolated from *C. ochotensis*, and its further characterization is reserved for a publication dealing with that plant. A small amount of the alkaloid ($-\nu$), giving analytical figures in agreement with $C_{19}H_{17}O_6N$, was present. It appears to be phenolic and probably lactonic. Methoxyl is absent, although an N-methyl group is present. The sixth alkaloid, for which the name *chrycentrine* is now proposed, also appears to be new. It is non-phenolic and probably contains two methylene-dioxy groups, but methoxyl groups are absent. Its empirical formula, $C_{18}H_{15}O_5N$, probably relegates it to the rapidly increasing group of Fumariaceous alkaloids containing five oxygen atoms. Three members of this series, which evidently does not include the structural features of the protopine group, were recorded in a communication dealing with *Corydalis sibirica* (3).

In the case of *D. ochroleuca*, there was available only one kilo of dried material, and the difficulty of a thorough examination was enhanced by the very low content of total alkaloids. Although indications of the presence

of other alkaloids are not lacking, bicuculline, protopine, and cryptopine are the only ones obtained in a state of purity.

It is relevant finally to mention an examination of *D. spectabilis* with the object in view of securing for identification the alkaloid melting at 142° C., which Danckwortt (1) isolated from this source. No alkaloid other than protopine could be isolated from 3.2 kilos of dried material of which the roots constituted 1.2 kilos. All fractions were carefully examined and the ultimate uncrystallized residue weighed only a few milligrams. Fumaric acid was particularly abundant in the aerial portion and its presence in *D. chrysantha* and *D. ochroleuca* was readily demonstrated.

Experimental

The procedure repeatedly employed by the author, and first detailed in the case of *Adlumia fungosa* (2), was used for separating the total alkaloids into a number of fractions. It may be added here that chloroform extraction of the aqueous acid solution (*S*) is most conveniently accomplished when it is not too dilute. A convenient concentration is such that a litre of solution is prepared from each kilo of plant material. In most cases separation of the two liquid phases is rapid and well defined, although the first addition of the chloroform generally causes the separation of a resinous product soluble in neither medium. When the amount is small its presence may be disregarded since it adheres to the walls of the separatory funnel. Larger quantities are desirably removed by filtration.

There was available six kilos of dried *D. chrysantha*, of which the roots constituted 1.5 kilos. The total dry material of *D. ochroleuca* weighed one kilo. The author is greatly indebted to Dr. Carl B. Wolf, Director of the Santa Ana Botanical Gardens, Anaheim, California, through whose kindness these materials were made available.

Isolation of Bicuculline from D. chrysantha

The amorphous dark fraction (*BC*) was dissolved in hot methanol and the filtered solution (charcoal) evaporated to a thin syrup. In the course of several days a small crystal nucleus had appeared, and when this was broken up with a rod rapid crystallization ensued. After filtering and washing, this alkaloid melted indefinitely at 185° C.* After one recrystallization from chloroform-methanol it melted at 194° C. A mixture of the product with the high melting form of bicuculline (m.p. 196° C.) melted at 195° C. The identity with bicuculline was further established by solution in hot chloroform, evaporation to a syrup, and addition of hot methanol, together with a nucleus of bicuculline (m.p. 177° C.). Crystallization was immediate and the bicuculline then melted at 177° C., either alone or in admixture with an authentic specimen. The yield was 1.9 gm. (0.03%).

In the case of *D. ochroleuca* the crude bicuculline melted at 175° to 177° C. solidified on further heating, and remelted at 193° C. After one recrystalliza-

* *All melting points are corrected.*

tion as above, it melted sharply at 177° C., and this melting point was not depressed when the alkaloid was admixed with an authentic specimen of bicuculline. The yield was 0.05%.

Isolation of Chrycentrine

The filtrate from the crude bicuculline was acidified with hydrochloric acid, water added, and the methanol boiled off. The filtered aqueous solution was basified with ammonia and the liberated base extracted with much ether. An insoluble resin separated on the walls of the separatory funnel. It was separately recovered by extraction with chloroform. During the evaporation of the ether extract to a small volume a sparingly soluble base crystallized. It was dissolved in hot chloroform in which it is sparingly soluble, and the solution was evaporated to a small volume. The addition of methanol yielded colorless stout prisms which melt at 216° C. Concentrated sulphuric acid dissolves this alkaloid to form a pale yellow solution, which on warming changed to brown, then to pink and on further heating to olive. With 80% sulphuric acid and phloroglucinol at 100° C., it yielded a red precipitate characteristic of the methylene-dioxy group. The yield of *chrycentrine* was about 0.01 gm., which included a small amount of the same alkaloid obtained from the chloroform extract of the ether-insoluble resin. Calcd. for $C_{18}H_{15}O_5N$: C, 66.48; H, 4.62; N, 4.31%. Found: C, 65.33; H, 4.75; N, 4.16% (means of duplicates).

The mother liquors from the crystallization of the chrycentrine were combined and redissolved in dilute hydrochloric acid. The bases were regenerated by adding excess potassium hydroxide and extracting with ether. The residue from the extract, in contact with a little methanol, deposited a small amount of crystalline material. This melted indefinitely at 220° C. When recrystallized from chloroform-methanol it was obtained in colorless stout prisms, which melted at 223° C. In appearance, solubility, and melting point this base is identical with an alkaloid isolated in relatively larger quantity from *Corydalis ochotensis*, and admixture of the two caused no depression in melting point.

Isolation of Alkaloid-ν

The ether extract representing fraction (*EC*) was freed of solvent, dried, and moistened with methanol. The crude crystalline material thus obtained melted at about 220° C. It was recrystallized from chloroform-methanol, and it then consisted of well formed stout prisms melting at 230° C. Calcd. for $C_{19}H_{17}O_5N$; C, 64.23; H, 4.79; N, 3.94%. Found: C, 65.25; H, 4.62; N, 4.01%.

Isolation of Protopine and Cryptopine

The isolation of protopine from fraction (*BS*) and as a contaminant from (*ES*) has been repeatedly described. In the case of *D. chrysantha* the yield was 0.17%, and in the case of *D. ochroleuca* it was 0.22%. The methanolic mother liquors from both sources were largely freed of solvent and rendered just acid by the addition of hydrobromic acid. During the course of several

days the characteristic pearly lustrous plates of cryptopine hydrobromide separated from both solutions. Regeneration of the free bases and recrystallization from chloroform-methanol yielded pure cryptopine which in each case melted at 221° C., and admixture with authentic cryptopine did not lower these melting points.

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AN INVESTIGATION OF THE CHLORINATION OF SPRUCE WOOD AND OF THE RESULTING CHLOROLIGNIN[1]

BY G. V. JANSEN[2] AND J. W. BAIN[3]

Abstract

Spruce sawdust was chlorinated under various conditions in an attempt to procure a homogeneous lignin chloride. Success finally attended the use of methyl alcohol as a medium for chlorination. The lignin chloride, which was dissolved by the alcohol during the chlorination and subsequently precipitated by the addition of water, was cream white in color, and analysis showed it to be an alcohol lignin.

A homogeneous fraction (No. 2) was obtained from the re-chlorinated product, and it proved to be a chlorinated analogue of Hibbert's monomethylated methyl alcohol lignin, the formulas of the two products being $C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$, and $C_{42}H_{32}O_6(OH)_2(OCH_3)_7$. The molecular weight and the presence of the two hydroxyl groups were confirmed by acetylation, when 2.0 acetyl groups entered the molecule. Eleven of the chlorine atoms in Fraction 2 have evidently replaced ten hydrogen atoms and one hydroxyl group by simple substitution in methyl alcohol lignin, leaving two chlorine atoms which have apparently entered to saturate a double bond. Seven of these chlorine atoms have been shown to be readily removable either by an alkali or by acid reduction. The other six, because of their stable union with the molecule, are surmised to be joined to an aromatic nucleus or at least to some type of ring structure. The product has been shown to react stoichiometrically within limits as narrow as could be expected for such a large molecule.

Introduction

One of the less severe methods by which lignin can be isolated from wood was discovered by Cross and Bevan in 1880 (3). They chlorinated moist jute fibre and extracted the chlorinated lignin with hot alcohol, from which solution it was precipitated by dilution with water as a yellow amorphous powder. This paper deals with an investigation of this method of isolating lignin and of the chlorolignin so obtained. The results of other investigators who have studied the halogenation of wood or lignin are briefly summarized in the following section.

Cross and Bevan (3) invariably obtained, from the chlorination of moist jute, a lignin chloride of the composition represented by $C_{19}H_{18}Cl_4O_9$ (Cl, 26.8%). The amount of hydrochloric acid formed was equivalent to the chlorine absorbed. This denoted simple substitution of hydrogen by chlorine. However, for fibres other than jute, hydrochloric acid was formed in excess; this showed that oxidation had taken place (5, p. 105). On further chlorination in acetic acid solution (4), the substance $C_{38}H_{44}Cl_{11}O_{18}$ was obtained (Cl, 34%).

Heuser and Sieber (15) chlorinated moist pine sawdust and found that 32% of hydrochloric acid was formed, whereas only 9.47% of chlorine combined with the wood. (These percentages refer to the weight of dry wood used, as will all succeeding percentage figures unless otherwise specified.) By means of alcoholic extraction they obtained a substance that gave the following analysis: Cl, 22.68%; C, 47.03%; H, 4.59%. The yield was only 7.1%. (Pine and spruce contain about 30% lignin.)

Heuser and Casseus (14) found that dry spruce wood flour suspended in carbon tetrachloride was acted upon by chlorine; with moist wood the reaction was more rapid. They could extract all the lignin in either case by successive treatments with sodium sulphite solution. The chlorine absorbed amounted to 41% of the weight of the wood, as was found by Heuser and Sieber.

Waentig (26) chlorinated wood-meal suspended in water; he stated that no chlorination took place in the absence of moisture. By alcoholic extraction he obtained lignin chlorides in which the chlorine content varied 'from 25.5 to 38.9%, depending directly upon the duration and temperature of chlorination and the acidity (hydrochloric acid) of the chlorination medium.

Moreover, the chlorine content of the alcoholic extract from any one experiment was not uniform. A water soluble lignin chloride was also produced in which the chlorine content varied from 18.6 to 19.1%.

Recently Müller (19) extensively investigated chlorolignin. He chlorinated moist pine sawdust and extracted the still moist wood, which then contained hydrochloric acid, with boiling 90% alcohol. If the wood were washed free of acid before extraction, only a small yield of lignin was obtained. This showed that a hydrolytic cleavage of the ligno-cellulose bond was necessary. The chlorinated lignin was precipitated as a golden brown colloid when the alcoholic solution was diluted with water. Müller separated the lignin chloride into two fractions by ether extraction:

(1) Ether insoluble lignin chloride, Cl, 23.1; OCH_3, 4.5%.
(2) Ether soluble chlororesin, so called because it resembled resin in appearance; Cl, 28.6; OCH_3, 4.8%.

Extraction of the lignin chlorides with water, hydrolysis (acid or alkaline), oxidation with potassium permanganate, or dry distillation, yielded no information as to their structure. However, alkali fusion yielded succinic acid and terephthalic acid as degradation products, and Müller considers that this indicates that in lignin there is a benzene ring containing two adjacent carboxyl groups. He also prepared a monoamide of chlororesin, and thus confirmed the presence of at least one carboxyl group in lignin.

Powell and Whittaker (22, 23) chlorinated alkali lignin obtained from various woods, and found that 12 chlorine atoms entered the lignin molecule. On solution in alkali and reprecipitation with acid, six chlorine atoms were split off. They give the following formulas for these bodies:

Dodecachlorolignin—$C_{40}H_{20}O_8Cl_{12}(OH)_6OCH_3CHO$; Cl, 35.1 to 35.5%.

Hexachlorolignin—$C_{43}H_{38}O_{16}Cl_6$; Cl, 20.4 to 20.8%.

Taylor, Maass and Hibbert (25) studied the mechanism of aqueous halogenation of several unsaturated compounds, using hypochlorous and hypobromous acids and various catalysts. They have shown that the addition of these acids to a double bond is in general catalyzed by undissociated hydrochloric and hydrobromic acids. They also studied the aqueous halogenation of phenols under the above conditions. Applying like methods to an investigation of the reaction of hypochlorous acid on glycol-lignin, Hibbert and Taylor (17) conclude that there is about 15% of a phenol nucleus in lignin, which accounts for about one-third of the rapid absorption of hypochlorous acid observed. The remainder they ascribe to the addition of hypochlorous acid to an ethylene linkage, chlorination of a phenol ether, or a combination of both reactions.

Some of the results of work done on the bromination of wood and lignin are of interest in connection with this paper and will be briefly outlined. Fuchs (9, 10, 11,) brominated spruce wood, Willstätter lignin, and acetylated spruce wood, and concluded that primary lignin contains a hydrogen atom that is replaceable by bromine and a double bond capable of addition of two bromine atoms, and that acetate lignin contains a tetrahydro benzene ring. Hibbert and Sankey (16) also found that lignin contained one or more double bonds per mole. Rassow and Zickman (24), on the other hand, conclude that there are no double bonds in Willstätter lignin. Friedrich and Pelikan (8) brominated lignin, extracted by acetic acid, in alcohol, acetic acid, and alkali solution. In alcohol solution, only an addition of bromine occurred and no methoxyl was split off. In alkali solution extensive oxidation took place, but in acetic acid a maximum bromine content of 38.7% was reached in 12 hr. Since the methoxyl content had dropped from 15.5 to 10.6% they concluded that the methoxyl groups in lignin are not all of the same type, and that the methoxyl groups split off during bromination remain as hydroxyl groups.

It can be seen that there is considerable disagreement in the results summarized above, and that no two of the various empirical formulas proposed for lignin agree. Nor does any one of these formulas for a lignin isolated by chlorination or bromination bear a close resemblance to those for lignin isolated by any of the other well known methods. However, by means of a suitable method of chlorination, the authors have succeeded in isolating a lignin fraction that appears to be a chlorinated derivative of Hibbert's monomethylated alcohol lignin.

General Procedure

Ontario white spruce only was used in the work described below. It was ground to pass a 100 mesh screen and extracted with a minimum boiling point mixture of benzene and ethyl alcohol for 20 hr. to free it from resins. After air-drying, its moisture content was determined and the dry weight calculated. It was then placed in the chlorinating apparatus, being either bone-dried or well moistened before chlorination.

Two types of chlorinating apparatus were used. The apparatus used first is shown in Fig. 1. Either pure chlorine gas or chlorine diluted with air, to keep the temperature low, could be drawn through the wood. Cooling to 0° C. could be achieved by the admission of ether or chloroform through the dropping funnel. (In these cases the wood was moistened with sodium nitrate solution to prevent its freezing.) The gas stream was led through the water in the bottom of the suction flask so that the hydrochloric acid that it carried from the wood might be absorbed. The wood was water washed after each chlorination till free from chlorides, and the hydrochloric acid was then determined by titration after removal of the chlorine in the wash water by the addition of sodium thiosulphate.
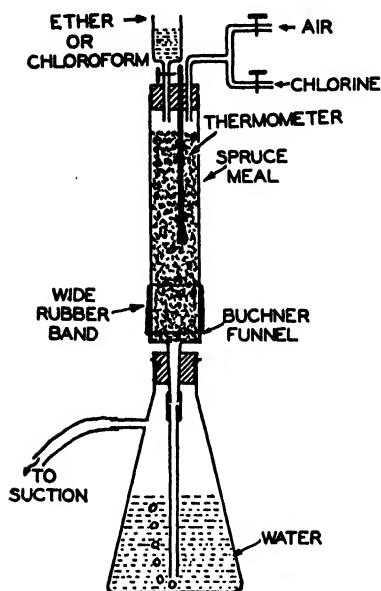
The wood was then extracted with alcohol in a Soxhlet for several hours, and the alcoholic solution of lignin chloride was concentrated by distillation *in vacuo*. In the experiments in which the water-soluble lignin chloride was determined, the water extraction of the chlorinated wood was performed first, under reduced pressure, and the lignin chloride was recovered by distilling

FIG. 1. *Apparatus for chlorination.*

off the water *in vacuo*. This process was repeated several times, four chlorinations and extractions being usually found sufficient to exhaust the wood of all alcohol soluble lignin chloride. The lignin chloride was recovered from the concentrated alcoholic solution by precipitation with cold water. It was purified by redissolving and reprecipitating two or three times, the precipitate being washed free of chlorides each time.

After the lignin was freed from hydrochloric acid and adsorbed chlorine, it was frequently found necessary to employ a concentrated solution of an inorganic salt like sodium sulphate, to throw it out of colloidal suspension in the diluted alcoholic solution. After a final thorough washing with water, it was air dried and its moisture content determined.

The product so obtained was analyzed for chlorine by the explosion method in a Parr peroxide bomb. In this method approximately 0.2 gm. of sample is placed in a Parr bomb together with 0.5 gm. of pure maltose, to supply the water necessary to start the combustion, and 10 gm. of sodium peroxide. The bomb is then heated for 20 sec. with a full Bunsen flame, allowed to cool for a minute or so, plunged into cold water and the contents then rinsed out with distilled water. The resulting alkaline solution is acidified with nitric acid, filtered, and the sodium chloride is precipitated with silver nitrate and weighed as silver chloride. This method, which is quite rapid, has been

shown to be quite as accurate as the time-consuming Carius method even for high melting solids (1). Typical analyses were: Cl: 28.50, 28.60; 30.55, 30.60; 27.25, 27.25%.

The results of some of these experiments with the first apparatus are listed in Table I.

TABLE I

Experiment No.	Temp. of chlorination, °C.	Conditions	Hydrochloric acid formed, %	Loss in wt. of wood, %	Chlorine in residual wood, %	Yield of lignin chloride, %	Chlorine in lignin chloride, %
1	40	No cooling, only gaseous chlorine used.				7.0	22.50
2	40	No cooling, only gaseous chlorine used.				11.0	24.30
3	40	No cooling, only gaseous chlorine used. Wood was not washed with water prior to alcoholic extraction.		30.7	2.3	17.2	1st extr. — 20.55 2nd extr. — 21.75 3rd extr. — 23.05 4th extr. — 24.75
4	30	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction.		16.0	3.0	4.9	14.6 to 18.6
5	0	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction.	45.9	18.7	5.4	6.0	1st extr. — 21.25 2nd extr. — 23.45 3rd extr. — 23.10
7	0	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction. Alcoholic extraction performed at reduced pressure.	33.0	17.4	6.6	6.4	1st extr. — 23.85 2nd extr. — 23.10 3rd extr. — 23.10 4th extr. — 23.40
8	30	Chlorine mixed with air. Wood washed free of chlorides prior to alcoholic extraction. Alcoholic extraction performed at reduced pressure.	34.1		4.0	6.4	1st extr. — 24.55 2nd extr. — 24.45 3rd extr. — 22.8 4th extr. — 23.5
9	50–60	Same as Experiment No. 3	96.5	20.9	4.4	13.4	1st extr. — 26.90 2nd extr. — 25.75
11	30	Same as Experiment No. 3		25.2	3.4	15.7	24.05

Discussion

The results in Table I are very similar to those obtained by Waentig (26) for his six hour chlorinations in a water medium, in which he obtained in 9% yield a lignin chloride with a chlorine content varying between 25.5 and 27.2%. As he concludes, the chlorine content of the lignin chloride varies with the chlorination temperature, the acidity, the duration of chlorination, and, to a certain extent, with the method of handling.

The amount of hydrochloric acid formed is high when no cooling is attempted, as would be expected. The greatest yields of lignin chloride were obtained in those experiments in which the wood was not water washed prior to alcoholic extraction. This showed that there is a considerable quantity of water soluble lignin chloride which is extracted during this process. That the chlorinated lignin cannot be completely extracted from wood by alcoholic extraction is shown by the fact that the residual wood invariably retains from 3 to 6% chlorine, which must be due to the lignin chloride it still contains.

The chlorine content of the water soluble lignin chloride obtained in Experiment 10 was 20.10%—lower than that of the alcoholic extract which was generally in the neighborhood of 24%.

The color of the lignin chloride seemed to vary also with the temperature of chlorination; that obtained from the chlorinations at 0° C. was bright yellow, whereas that obtained at higher temperatures was brown or gray. They all tended to darken on dry heating.

The product was soluble in alkali, ammonium hydroxide (dilute and concentrated), sodium carbonate solution (dilute and concentrated) and acetone (75% to absolute). It was partially soluble in glacial acetic acid, but on standing for some time it became insoluble in this reagent.

It was realized that conditions could not be controlled well enough to produce the same homogeneous product at will, so the apparatus shown in Fig. 2 was designed for chlorinating the wood in a liquid medium where the temperature could be better controlled, and local heating and attendant high oxidation eliminated.

Experiments with Apparatus No. 2

A chlorination was first attempted with dry wood flour (325 mesh) suspended in carbon tetrachloride. The wood absorbed 10.7% chlorine, but 26.7% of hydrochloric acid was formed. Considerable oxidation had therefore occurred. Less than 1% of the lignin chloride could be extracted by hot alcohol or acetone, and its chlorine content was not uniform, ranging from 13.5 to 32.5%. An experiment in which water soaked wood was used yielded more encouraging results; 20.6% of chlorine was absorbed and only 28% of hydrochloric acid was formed. This showed that little oxidation had taken place. The percentage of alcohol soluble lignin chloride recovered was 18, but this had a non-uniform chlorine content (28 to 32%). The methoxyl content of the

FIG. 2. *Apparatus for chlorination on a large scale.*

product was approximately 8.5% on a chlorine-free basis. Therefore, about one-half of the methoxyl content had been lost during chlorination (17% OCH$_3$ is the value assigned to spruce lignin by Brauns and Hibbert (2)).

Experiments on Chlorination in Methyl Alcohol

Since Friedrich and Pelikan (8) stated that they had obtained only an addition of bromine with no loss of methoxyl on brominating their lignin in alcohol, it was decided to try methyl alcohol as a medium for the chlorination of wood. The result was quite remarkable.

Air-dry wood (100 gm., 5% moisture content) was placed in 800 cc. of methyl alcohol and chlorinated for 48 hr. Neither the wood nor the alcohol was thoroughly dried, because it was desired to have a small amount of water present to facilitate the chlorination and increase the yield of lignin chloride, and it was felt that by using just this minimum amount, dissolved as it would be in the methyl alcohol, oxidation would be virtually eliminated.

After chlorination, the wood, which was still light yellow in color rather than orange (as in all previous experiments with moist wood), was filtered from the alcohol, washed free of chlorides, dried, and extracted with acetone *in vacuo*. This extraction yielded a cream yellow colored product (Cl, 29.6%) on precipitation with water. It was not possible to determine the amount of hydrochloric acid formed in this experiment, since the methyl alcohol was attacked by the chlorine.

The alcohol, which had been used for a chlorination medium, yielded an even lighter colored precipitate on addition of water, its color being virtually pure white and its chlorine content 28.8%. No other investigator has ever reported, to the authors' knowledge, a white colored lignin product. Alkali lignin perhaps comes the closest to this, being very light yellow. Grüss claims to have prepared a white crystalline lignin of formula $C_{26}H_{46}O_{10}$ (C, 60.2; H, 8:9%), by refluxing wood wet with hydrochloric acid solution with ethyl alcohol. However, Friedrich and Brüda (6) (see also (7)), though using this method to prepare their primary lignin, obtained a cocoa-brown colored product of empirical formula $C_{39}H_{48}O_{14}$ (C, 63.3; H, 6.5%). This analysis falls within the range generally given for lignin, whereas Grüss' compound is rather low in carbon and much too high in hydrogen. Grüss' "crystalline lignin" has hence never been reproduced. He did not give its methoxyl content. Friedrich and Diwald (7) gave 20.9% as the methoxyl content of their primary lignin, but Hägglund and Rosenquist (12) showed that part of this was due to ethoxyl, their product being a compound of ethyl alcohol and lignin or an "alcohol lignin" similar to the glycol lignins Hibbert and co-workers have recently been investigating (25). Calculated on the true weight of the lignin (less the ethoxyl part), the methoxyl content of primary lignin then becomes 14.0%, which is similar to the methoxyl content of Willstätter lignin. If the ethoxyl be replaced by methoxyl and the total methoxyl content be then considered, the methoxyl content would be 22.6%—

Brauns and Hibbert give as the methoxyl content of their methyl alcohol lignin 21.45%.

A further 12 hr. chlorination of the extracted wood in methyl alcohol yielded a white lignin chloride (Cl, 35.6%). The methoxyl content of the first extract of this white lignin chloride was 15.9%. Calculated on a chlorine-free basis (on the assumption that the chlorine atoms have replaced hydrogen atoms), this would be 22.1%, which indicated that this product was also an "alcohol lignin". However, the temperature required for its isolation is certainly much lower than that used in other methods for preparing such products, all those so far published depending on treatment of the wood with hot or boiling solvent plus hydrochloric acid for several hours, the resulting compound of lignin plus solvent being darker in color than that of the authors' (yellow, brown or gray).

The methoxyl content of the acetone extract was also high, *viz.*, 15.5, or 21.8% on a chlorine-free basis, so that evidently the alcohol combined with the lignin before it had been extracted from the wood.

Experiment on Alcohol Lignin Chloride

Air-dry wood (700 gm.) was chlorinated in methyl alcohol for a total period of three weeks. During this time the wood was allowed to settle about every four days and the supernatant layer of alcohol was siphoned off, the lignin that it contained being precipitated with cold water. The fifth extract yielded virtually no lignin, so the chlorination was assumed to be completed.

These extracts were united and washed with distilled water on a Büchner funnel till free of chlorides. The yield of crude, air-dry product was 122 gm., or 16.5% on a dry basis. The product was then redissolved in acetone and reprecipitated to further purify it. The only successful way of precipitating the lignin from this concentrated acetone solution was to dilute it with alcohol and then quickly add cold tap water, small portions being treated successively in this manner. If water was added directly to the acetone solution a brown, resinous mass came down, which, however, could be again obtained as the white product by the above technique of precipitation.

The product was then dried *in vacuo* over phosphorus pentoxide, and was further purified by redissolving it in acetone and precipitating it by the addition of carbon tetrachloride and then petroleum ether. The addition of petroleum ether alone again yielded a brown, gummy precipitate. A cream-white colored product (Cl, 29.8%) was thus obtained, the final yield being 55 gm. or about 8%.

The material was not homogeneous, as was shown by the analysis of two fractions obtained by adding carbon tetrachloride to an acetone solution, filtering and obtaining a second precipitate by the addition of petroleum ether. The chlorine contents of the two fractions were 27.4 and 30.0% respectively. Alcohol lignin chloride (20 gm.) was then rechlorinated in methyl alcohol for seven days. Most of the material, which had largely lost its solubility in this reagent during purification and drying, redissolved. The insoluble portion

was filtered off and the dissolved fraction recovered as before by precipitation with ice water. The chlorine content was now greater and much more uniform, as was shown by a test similar to that mentioned above, *viz.*: chlorine content of fraction precipitated by carbon tetrachloride, 31.5; chlorine content of fraction precipitated by petroleum ether, 31.9%. A second fractionation of the portion precipitated by petroleum ether yielded two fractions of almost identical chlorine content, namely 30.8 and 31.0%. Hence, it appeared that a homogeneous material could be obtained by fractional precipitation of the re-chlorinated alcohol lignin chloride, and to this end it was decided to prepare a large enough quantity of the substance to enable a thorough investigation of its properties to be carried out.

Preparation of a Homogeneous Fraction of Alcohol Lignin Chloride

Air-dry spruce sawdust (7 kg.) was chlorinated, as described, in methyl alcohol for a total period of about three weeks, the supernatant layer of alcoholic lignin chloride solution being withdrawn periodically and fresh alcohol being substituted. The crude alcohol lignin chloride was obtained by diluting the alcoholic solution with water. A total yield of 950 gm. (13.5%) of white air-dry product was obtained. This was then suspended in methyl alcohol and subjected to another chlorination period of 10 days, after which most of it had redissolved. The insoluble portion was filtered off and a final yield of about 500 gm. of re-chlorinated product was obtained on precipitation with water. The portion soluble in carbon tetrachloride was then extracted by refluxing the material with successive amounts of carbon tetrachloride until no more lignin dissolved, and the solutions were then united and concentrated by evaporation of the carbon tetrachloride *in vacuo*.

This carbon tetrachloride solution of alcohol lignin chloride was then precipitated, in four fractions, by the gradual addition of petroleum ether. It was found necessary to first dilute it again to about two litres to obtain the familiar creamy white, flocculent precipitate, as otherwise the lignin came down as a brown, scaly resin, similar, evidently to Müller's chlororesin. The fractions were then analyzed for chlorine, with results as shown in Table II.

Since Fractions 2 and 3 were of identical chlorine content, it was decided to analyze them further for car-

TABLE II

Fraction No.	Yield, gm.	Color	Chlorine content, %
1	13.2	Cream yellow	43.2
2	38.7	Cream white	35.35, 35.4
3	32.0	Cream white	35.30, 35.4
4	34.2	Cream yellow	37.4

TABLE III

	Fraction 2, %	Fraction 3, %
H_2O	6.00	6.65
C	43.01, 43.15	43.7, 43.8, 43.9
	Av. 43.1	Av. 43.8
H	3.40, 3.40	3.47, 3.45 (3.46)
OCH_3	16.95, 16.95	17.96, 17.92

bon and hydrogen to see whether they actually represented a strictly homogeneous fraction of lignin chloride. The complete analyses are given in Table III.

It can be seen that the carbon and hydrogen contents of Fraction 3 are slightly higher than those of Fraction 2, but this can be satisfactorily explained by the higher methoxyl content of Fraction 3. It is clear, from the high methoxyl content of these fractions, that we are dealing with an alcohol lignin, and that evidently more than one of the hydroxyl groups have been methylated by combination with the alcohol during the chlorination. The methoxyl content on a chlorine-free basis would be approximately 26%. Hibbert gives the methoxyl content of his methyl alcohol lignin as 21.45%; that of the mono-methylated product, 24.1%. Hence, it is clear that the lignin chloride has suffered methylation during its isolation and Fraction 3 has been slightly more highly methylated than Fraction 2. A comparison of the two fractions, after allowance is made for this difference in methoxyl, will show them to be virtually identical in composition (Table IV).

TABLE IV

ATOMS PER 100 GM. OF LIGNIN CHLORIDE

——	Fraction 2	Fraction 3	Fraction 3 (corr.)
C	3.56	3.61	3.58
H	3.40	3.46	3.40
Cl	0.997	0.996	0.996
OCH$_3$	0.547	0.579	0.547

It is seen that there are 0.032 excess methoxyl groups per 100 gm. of lignin in Fraction 3. Since this must have replaced hydroxyl groups, there should be 0.032 atoms of carbon and 0.064 atoms of hydrogen less in Fraction 3, if the two fractions are to be compared on the same methoxyl content basis. The results obtained after making this subtraction are shown in Table IV in the fourth colum, and it is apparent that the two fractions are now of identical composition. Hence, the authors felt justified in proceeding with the investigation of this lignin, since, except for a slight variation in its methoxyl content, it was strictly homogeneous and could be regarded as a definite compound of lignin.

Properties of Alcohol Lignin Chloride

Alcohol lignin chloride is an amorphous, creamy white colored powder, unchanged by heating at 110° C., but which gradually turns brown and melts at 160° to 170° C. and finally carbonizes at about 200° C. It is very soluble in acetone, ethyl acetate, acetic acid, acetaldeyhyde, propionic acid, chloroform, pyridine, quinoline, nitrobenzene, and alcohol plus benzene; completely soluble in 5 to 10% sodium hydroxide, ether plus alcohol, carbon tetrachloride, benzene plus ether, and alcoholic sodium hydroxide; partially soluble in ammonium hydroxide, dilute sodium hydroxide, absolute alcohol, and benzene; insoluble in water, sodium carbonate solution, methyl alcohol, 95% ethyl alcohol, ether, dilute nitric acid, concentrated hydrochloric acid and 50%

sulphuric acid. It has a characteristic varnish-like odor, and is slightly hygroscopic. All experiments were done with the air-dry material and corrected to a bone-dry basis. It is very difficult to dry thoroughly, requiring several days heating *in vacuo* at 80° to 90° C. before attaining a constant weight.

Formula of Alcohol Lignin Chloride

Fraction 2 was used throughout in the experiments described below, and of the various formulas that have been proposed for lignin, that of Hibbert's agrees best with the authors' results. Brauns and Hibbert (2) give as the empirical formula for native lignin, $C_{47}H_{52}O_{16}$, and state that it contains five hydroxyl and five methoxyl groups. In methyl alcohol lignin, one hydroxyl has been replaced by one methoxyl in the extraction process, and in the monomethylated methyl alcohol lignin (methylated with diazomethane) there are accordingly seven methoxyl groups. Fraction 2 seems to be akin to this monomethylated derivative as it also contains seven methoxyl groups, and the differences in the two formulas can be satisfactorily explained by the presence of the chlorine in the authors' preparation. The two formulas are given in Table V, and it will be seen that the authors' analytical and calculated results agree as well, if not better than Hibbert's.

TABLE V

	Fraction 2, alcohol lignin chloride $C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$, mol. wt., 1334		Hibbert's monomethyl alcohol lignin $C_{42}H_{32}O_6(OH)_3(OCH_3)_7$, mol. wt., 900	
	Found, %	Calculated, %	Found, %	Calculated, %
C	43.1	44.1	66.3	65.3
H	3.40	3.37	6.35	6.3
Cl	35.4	34.6	27.35	28.4
O	18.1	18.0	24.9	24.1
OCH₃	16.9	16.3		

It will be noticed that alcohol lignin chloride has 10 hydrogen atoms less than Hibbert's lignin and one hydroxyl group less. These have evidently been replaced by 11 chlorine atoms. There are still two chlorine atoms unaccounted for, which must have entered the molecule to saturate a double bond, as seems probable from the work of Fuchs, Hibbert and Sankey, and Friedrich and Pelikan, who all found lignin capable of addition of bromine.

Methylation of Alcohol Lignin Chloride

Methylation was first attempted with dimethyl sulphate in acetone solution with powdered calcium carbonate added to take up sulphuric acid, since it was feared that sodium hydroxide would split off chlorine from the lignin chloride. However, no further methylation resulted. With pyridine as the solvent, the same negative result was obtained. Sodium hydroxide was finally

used and the experiment carried out according to the procedure of Holmberg and Wintzell (18). The final product after filtering and washing was light brown and was obtained in 50% yield. It was analyzed for methoxyl and chlorine. Found: OCH_3, 19.1; Cl, 19.6%. Although the methoxyl content is higher than the original, this can be seen to be due solely to the loss of chlorine suffered during the methylation. Trial and error showed that the experimental results agreed best with the assumption that seven chlorine atoms had been replaced, and that the methoxyl content had remained unchanged, giving a substance of formula $C_{42}H_{28}O_6Cl_6(OH)_3(OCH_3)_7$. Calcd. for OCH_3, 19.5; Cl, 19.2%. Found: OCH_3, 19.1; Cl, 19.7%. This would mean that six chlorine atoms had been replaced by hydrogen atoms (a result analogous to Powell and Whittaker's findings on chlorinated alkali lignin), and one chlorine atom by a hydroxyl group, probably the same chlorine atom that had replaced a hydroxyl group during the original chlorination.

Acetylation of Lignin Chloride

Since the presence of two hydroxyl groups could not be demonstrated by methylation it was decided to try acetylation, and this proved more successful. Lignin chloride (3 gm.) was dissolved in 35 cc. of acetyl chloride and refluxed for 30 min. (22). The solution was cooled, diluted with acetic acid, and the lignin precipitated by dilution with water. The precipitate was white and seemingly unchanged in appearance. It was filtered, washed free of acid, air-dried, and its moisture content determined. Then the acetyl content was determined by the method of Ost and Katayama (20). In this method the acetyl groups are first hydrolyzed by strong acid or alkali, then the solution is diluted, and the free acetic acid is distilled off in steam, and titrated. Acid hydrolysis failed to yield any appreciable quantity of acetic acid, probably because the lignin would not dissolve in the 50% sulphuric acid used as a hydrolyzing agent. However, by the use of alkaline hydrolysis, a distillate was obtained which required 2.40 cc. of 0.218 N sodium hydroxide for an 0.5022 gm. sample of acetylated lignin. The distillate gave no precipitate with silver nitrate and nitric acid. This showed that no chlorine had distilled over. A blank determination run on the original lignin chloride gave a negative result, so it was evident that the lignin chloride had actually been acetylated. The moisture content of the acetylated lignin was 6.3%, so that its acetyl content was:

$$2.40 \times \frac{0.218}{1000} \times \frac{43}{0.5022} \times \frac{100}{93.7} \times 100 = 4.8\% \ .$$

The acetylated lignin was then analyzed for chlorine and methoxyl to make sure that these had not been split off during the acetylation. Found: Cl, 34.3; OCH_3, 15.7%.

The new values calculated on the assumption that the only change in the molecule was an addition of 4.8% of acetyl, *i.e.*, an increase in weight of $\frac{42}{43} \times 4.8 = 4.68\%$ (since one hydrogen atom is replaced by each acetyl

group entering), would be: Cl, $35.4 \times \dfrac{95.32}{100} = 33.8\%$; OCH_3, $16.9 \times \dfrac{95.32}{100} = 16.1\%$. These figures agree fairly well with the experimental values and show that neither chlorine nor methoxyl was replaced during the acetylation.

The new molecular weight of this acetylated lignin would be $1334 \times \dfrac{100}{95.32}$, and the number of acetyl groups which had entered the molecule $= 1334 \times \dfrac{100}{95.32} \times \dfrac{4.8}{43} \times \dfrac{1}{100} = 1.56$.

This figure should be very close to 2.0 if it is to agree with the formula chosen. It was felt that further acetylation might be obtained under different conditions, and experiment proved this to be so. One-half hour acetylation at room temperature gave the greatest value in a series of experiments in which the acetyl content was determined roughly by direct back-titration of the alkali solution used to hydrolyze the acetylated samples. A repeat experiment in which these conditions were used for the acetylation was accordingly performed and the acetyl content of the product was determined as before by steam distillation. The acetic acid in the distillate was determined by titration with $0.105\ N$ sodium hydroxide and bromcresol purple as an indicator. A blank was also run on 25 cc. of $0.0105\ N$ sodium acetate solution to determine what correction should be applied for the carbon dioxide dissolved in the distillate. The results are given in Table VI.

TABLE VI

Portion	Titrations of distillate from hydrolyzed lignin solution		Titrations of distillate from sodium acetate solution	
	Distillate, cc.	Titre, cc.	Distillate, cc.	Titre, cc.
First	600	2.45	700	2.68
Second	800	0.50	400	0.23
Third	600	0.40	300	0.17
Fourth	800	0.42	800	0.42

Weight of air-dry acetylated product, 0.198 gm.; moisture content, 7.0%.

It is obvious that all the acetic acid comes off in the first two portions of distillate. The titration for the sodium acetate blank should be 2.5 cc., hence the correction on 1100 cc. of distillate is 0.41 cc. ($2.91 - 2.50$).

Therefore the correction for the first two portions of the distillate from lignin solution (1400 cc.) is 0.52 cc. $\left(\dfrac{0.41 \times 1400}{1100}\right)$

The corrected titration is, 2.43 cc. (2.95 − 0.52).   Then the percentage of acetyl in the 0.198 gm. sample of acetylated lignin is,

$$\frac{2.43 \times 0.105 \times 43 \times 100 \times 100}{0.198 \times 1000 \times 93} = 5.97 .$$

$\frac{42}{43} \times 5.97 = 5.82\% =$ increase in molecular weight.

Hence the number of acetyl groups that have entered the molecule is,

$$\frac{1334}{43} \times \frac{100}{94.18} \times \frac{5.97}{100} = 1.97 \text{ or } 2.0 .$$

This is excellent evidence that the formula chosen for alcohol lignin chloride is correct, since the presence of two hydroxyl groups is confirmed.

Reduction of Alcohol Lignin Chloride

About 10 gm. of lignin was dissolved in 150 cc. of glacial acetic acid and placed in a flask with granulated zinc.   Water (20 cc.) was added to facilitate the evolution of hydrogen and the whole left at 40° C. for a week.   The solution turned from golden brown to black.   The lignin was then recovered by precipitation with water, washed free of acid, and air-dried.   Yield, 3 gm.   It was still white in color and apparently unchanged.   A complete analysis was made; the results are given in Table VII.

It is evident that both chlorine and methoxyl were removed during the reduction, and that at the same time the lignin underwent some acetylation from contact with the acetic acid.   The reaction may be represented as:

$$C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7 + CH_3COOH + H_2 + H_2O \longrightarrow$$

$$C_{42}H_{28}O_6Cl_6(OH)_4(OCH_3)_5\left(CH_3C\diagup_{\diagdown O}^{O}\right) \text{(mol. wt., 1123)}.$$
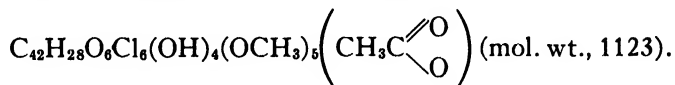
TABLE VII
ANALYSIS OF REDUCED LIGNIN CHLORIDE

	Found, %	Calculated, %
C	51.0	52.3
H	4.46	4.45
Cl	20.1	19.0
OCH$_3$	13.8	13.8
CH$_3$CO	3.75	3.83
O	24.3	24.2

·Seven chlorine atoms had been removed, six having been replaced by hydrogen atoms and one by a hydroxyl group.   This is exactly what happened in the methylation experiment above, so that evidently seven of the chlorine atoms in lignin chloride are readily removed either by alkali or by acid reduction, the other six being firmly bound probably to an aromatic nucleus.

In addition to the removal of chlorine, however, two methoxyl groups have been hydrolyzed off, one being replaced by hydroxyl and the other by acetoxyl, $CH_3C\underset{\diagdown O-}{\overset{\diagup O}{}}$.

The chlorine content is slightly higher than the calculated value for six chlorine atoms. This tends to suggest that the reduction had not gone quite to completion. This was further shown to be the case by fractional precipitation of a sample of the reduced lignin from acetone solution by the gradual addition of alcohol and water. Two fractions were collected and analyzed for chlorine, (1), 19.9; (2), 20.5%. This result showed that the chlorine content was not quite homogeneous throughout the reduced lignin, probably because the reaction had not been allowed to continue long enough to completely remove the seven atoms of chlorine.

Although many other experiments suggested themselves which might have been performed on this chlorinated product of lignin, time did not permit the authors to continue the investigation. However, enough had been done to demonstrate that the body did react stoichiometrically within limits as narrow as could be expected for such a large molecule, and that it confirmed Hibbert's general formula for lignin.

Portion Insoluble in Carbon Tetrachloride

Since more than 200 gm. of the original lignin chloride remained as a residue insoluble in carbon tetrachloride, this portion was separated into three fractions for the use of future investigators, and one fraction was completely analyzed as a matter of interest to see how its constitution compared with that of the portion soluble in carbon tetrachloride.

The product was dissolved in acetone, and a fraction precipitated by the addition of carbon tetrachloride. This fraction came down as a brownish resin, and it was filtered off and dried. Yield, 74 gm. of an orange brown, brittle, resinous-looking material. A second fraction (1A) was obtained by the addition of more carbon tetrachloride to the original solution, and a third fraction (1B) was precipitated by the addition of petroleum ether to the mother liquor. 1A was yellowish white in color (Cl, 34.5%; yield, 44 gm.); 1B was cream white in color (Cl, 32.0%; yield, 84 gm.). Fraction 1B was then analyzed completely, and was also tested for homogeneity. A portion was dissolved in acetone, and, by the gradual addition of carbon tetrachloride and petroleum ether, three fractions were precipitated successively. Upon analysis these gave the following chlorine contents: (i) 31.2, (ii) 32.3, (iii) 32.7%; accordingly Fraction 1B was not strictly homogeneous.

TABLE VIII

ANALYSIS OF FRACTION 1B

	Found, %	Calculated, %
C	49.4	48.0
H	3.56	3.58
O	16.0	15.0
Cl	32.0	32.5
OCH₃	15.4	15.5

However, its analysis gives a clue to its average constitution, and shows its relation to the fraction soluble in carbon tetrachloride (Fraction 2, Table V).

The average constitution of Fraction 1B is represented fairly accurately by the empirical formula $C_{48}H_{43}O_{12}Cl_{11}$.

The formulas of Fractions 1B and 2, Table V, may now be compared along with Hibbert's formula for native lignin:

Hibbert's native lignin—$C_{42}H_{32}O_6(OH)_5(OCH_3)_5$

Fraction (2) —$C_{42}H_{22}O_6Cl_{13}(OH)_2(OCH_3)_7$

Fraction 1B —$C_{42}H_{25}O_6Cl_{11}(OCH_3)_6$.

It is seen that Fraction 1B is quite different from No. 2. Only one hydroxyl group has been methylated during the chlorination and just 11 chlorine atoms have entered the molecule. Seven of these chlorine atoms have evidently replaced seven hydrogen atoms, and the other four have gone to replace the remaining four hydroxyl groups, leaving the product free of hydroxyl groups. The future investigation of this body should accordingly prove very interesting.

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FREE RADICALS IN ORGANIC DECOMPOSITION REACTIONS

I. THE THERMAL DECOMPOSITION OF MIXTURES OF METHYL ETHER AND DEUTERO-ACETONE[1]

By E. W. R. Steacie[2] and W. A. Alexander[3]

Abstract

A new method of obtaining information concerning the participation of free radicals in decomposition reactions is described. A mixture of two organic compounds is decomposed, all the hydrogen in one of the compounds having been replaced by deuterium. By an examination of the distribution of deuterium among the products, it is possible to obtain considerable insight into the mechanism of the process.

Mixtures of deutero-acetone and dimethyl ether have been decomposed at 590° C. It is found that the hydrogen in the products is entirely "light" within the experimental error. This precludes the possibility that formaldehyde (which is the source of the hydrogen) decomposes by a free radical mechanism, HCHO = H + CHO, as otherwise reaction of hydrogen atoms with deutero-acetone would lead to the formation of HD.

It is also concluded that it is unlikely that formaldehyde formed in the methyl ether decomposition is decomposed by sensitization from methyl radicals from the ether decomposition. If this were the case we would expect to have the reactions

$$CH_3 + HCHO = CH_4 + CHO$$
$$CHO = CO + H,$$
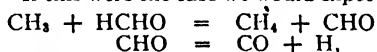
and again hydrogen atoms by reaction with deutero-acetone would yield HD.

The method of investigation seems to have interesting possibilities and to be of wide applicability.

Introduction

There is at present considerable uncertainty regarding the importance of free radicals in organic decomposition reactions. Information on this point is particularly desirable in the case of substances which decompose by a first order mechanism, in view of the suggestion of Rice and Herzfeld (18) that practically all first order reactions might really be chain processes involving atoms and radicals.

Experimental information on this point is available from various sources. The work of Rice and his collaborators, following up the original discovery of Paneth and Hofeditz (14), has definitely established the production of free radicals in large quantities when various organic compounds are heated to temperatures between 800° and 1000° C. (20). Rice and Herzfeld showed that it was possible to construct reasonable mechanisms on a free radical chain basis which would lead to agreement with the observed kinetics of decomposition reactions.

Striking support for the Rice-Herzfeld mechanisms was immediately forthcoming. Frey (6) was able to start chains in *n*-butane at temperatures below its normal decomposition range by adding methyl radicals produced by the decomposition of dimethyl mercury. Similarly Allen and Sickman (2, 23) were able to initiate chain decomposition in acetaldehyde with methyl

radicals from the decomposition of azomethane. Leermakers (13) also produced sensitized chain decomposition of methyl ether at temperatures below 400° C. by photolyzing admixed acetone. All these researches prove that radicals *can* cause chain decomposition of a large number of organic substances. They do not, however, necessarily prove that such free radical chains occur in the normal pyrolysis of the substances concerned.

Further evidence for the chain character of a number of decomposition reactions is furnished by the work of Staveley and Hinshelwood (24, 25, 26). They found that while large amounts of nitric oxide will catalyze numerous reactions, small amounts cause some inhibition. They assume that the maximum inhibition corresponds to a complete suppression of chains normally present, and thus calculate chain lengths of from two to four for the decomposition of diethyl ether, propionaldehyde, and ethyl propyl ether. If their conclusions are correct this is evidence for chains, but is definitely evidence against the Rice-Herzfeld scheme, since the chain lengths found experimentally are far too small. However, the assumption that maximum inhibition corresponds to a complete suppression of all chains is extremely arbitrary, and makes the calculated chain lengths of little real significance.

On the other hand, rather definite evidence against the radical chain theory is furnished by the work of Patat and Sachsse (15, 16, 17, 22). They measured the rate of the ortho-para hydrogen conversion in the presence of decomposing organic compounds, and were thus able to detect hydrogen atoms produced by the decomposition or by the reaction

$$CH_3 + H_2 = CH_4 + H . \qquad\qquad (A)$$

In general, the hydrogen atoms produced in this way are being destroyed by the reaction

$$H + RH = H_2 + R , \qquad\qquad (B)$$
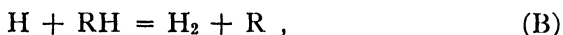
where RH is an organic molecule and R a free radical. Hence the stationary concentration of hydrogen atoms is defined by the two processes and we get approximately

$$(CH_3)/(H) = k_B(RH)/k_A(H_2) .$$

Having evaluated the hydrogen atom concentration by means of the rate of the ortho-para hydrogen conversion, we can thus calculate the concentration of methyl radicals and compare it with the value calculated from the Rice-Herzfeld mechanism. In general, using the activation energies assigned to the above reactions by Rice and Herzfeld, Patat and Sachsse find the hydrogen atom concentrations to be lower, by several powers of 10, than those calculated from the free radical chain theory.

Another way of testing the theory is to determine in an independent way the activation energies of one or more of the part reactions in the Rice-Herzfeld mechanism for a given substance, and compare them with those assigned in order to obtain agreement with experiment for the over-all reaction.

In the case of the ethane decomposition, for example, one of the fundamental steps in the free radical mechanism is (18)

$$H + C_2H_6 = H_2 + C_2H_5 . \qquad E = 17 \text{ Kcal.}$$

Steacie and Phillips (28) investigated this reaction by the atomic deuterium method and estimated the activation energy to be 6.3 Kcal. If we use this value instead of 17 Kcal., the Rice-Herzfeld mechanism no longer predicts the correct order or over-all activation energy for the ethane decomposition.

It follows from the above discussion that the existing experimental evidence concerning the participation of free radicals in organic decomposition reactions is inconclusive and somewhat conflicting. It is therefore desirable to search for other methods of investigation which may throw some light on the problem. With this end in view, experiments have been carried out in which a mixture of two organic compounds is decomposed. In one of these compounds all the hydrogen atoms have been replaced by deuterium. If decomposition occurs by a molecular mechanism, the products of the decomposition of one compound should be entirely "heavy," while those of the other are entirely "light." If, however, free radicals or atoms intervene, then cross-products will be formed. It is therefore possible to obtain considerable information concerning the mechanism of the decomposition from an examination of the distribution of deuterium among the products. The present communication describes experiments of this sort with mixtures of dimethyl ether and deutero-acetone.

It is known that the products formed in the decomposition of these two substances are mainly those indicated by the equations:

$$CH_3OCH_3 = CH_4 + HCHO$$
$$= CH_4 + H_2 + CO \ (10),$$
$$CH_3COCH_3 = CH_4 + CH_2 = CO$$
$$= CH_4 + CO + \tfrac{1}{2} C_2H_4 \ (11, 21, 30, 31).$$
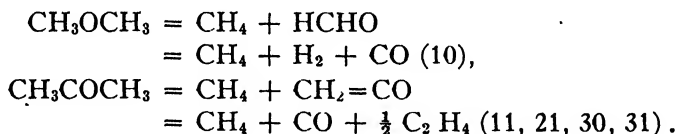
The decomposition of acetone is not as smooth as that of methyl ether, and the products are not in exact agreement with the above equation. However, the important thing for our purpose is that very little hydrogen is formed (about 2%). Hence, virtually all the hydrogen formed in the pyrolysis of a mixture of methyl ether and acetone arises from the methyl ether.

If, therefore, the reactions proceed by a molecular mechanism, we should expect on decomposing a mixture of methyl ether and deutero-acetone to find that the resulting hydrogen was almost entirely "light." On the other hand, if the formaldehyde from the ether decomposition itself decomposes by a free radical mechanism, we should have (15)

$$HCHO = H + CHO$$
$$CHO = CO + H$$
$$H + HCHO = H_2 + CHO$$
$$\text{etc.,}$$
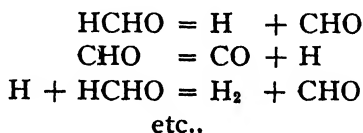
a reaction chain being set up.   In the presence of deutero-acetone, however, the reaction

$$H + CD_3COCD_3 = HD + CD_2COCD_3$$
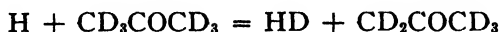
can also occur, and the hydrogen in the products should be deuterized to a considerable extent.   We can thus determine whether or not free hydrogen atoms have appeared during the decomposition process by analyzing the hydrogen formed.

It should be mentioned that at the temperature employed in this work (590° C.) methyl ether decomposes about five times faster than acetone. Hence, when formaldehyde is decomposing there will always be available ample acetone to react with any hydrogen atoms which may be formed.

Experimental

Apparatus

The apparatus is illustrated in Fig. 1.   The pumping system (not shown) was of the usual type, consisting of a rotary oil pump, a mercury vapor pump, and liquid air traps.   The left-hand section of the apparatus, consisting of
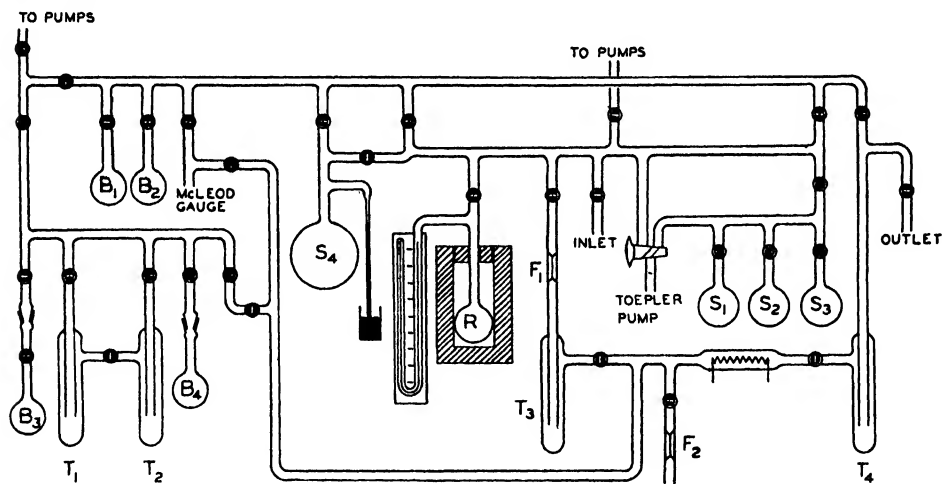
FIG. 1.   *Diagram of apparatus.*

bulbs B_1, B_2, B_3, and B_4, and traps T_1 and T_2, was used for the preparation, distillation, and storage of deutero-acetone, as described later.   Dimethyl ether was introduced into the apparatus through the tube marked "Inlet" and was stored in bulb S_1.   Mixtures of acetone and ether were made up and stored in S_4.   The reactants were decomposed in the fused silica reaction vessel, R, of 500 cc. capacity.   This was connected to the apparatus and to a capillary manometer through a quartz to soft glass graded seal.   The manometer and connecting tubing attached to the reaction vessel were wound with nichrome wire and electrically heated to prevent condensation.   The reaction vessel was surrounded by an electric furnace, the temperature of which was controlled by hand regulation of rheostats.   Temperatures were measured by means of a chromel-alumel thermocouple in conjunction with a

Cambridge thermocouple potentiometer. The temperature could be maintained constant to within $\pm$ 2°. All runs were made at 590° C. and with a 1:1 mixture of ether and acetone. The initial pressure of the reaction mixture was approximately 20 cm. throughout.

After the reaction had proceeded for the desired time, the reaction products were transferred by means of a Toepler pump to the storage bulbs S_2 and S_3. In order to obtain sufficient products for analysis, it was necessary to make several decompositions under identical conditions and combine the products in the storage bulbs.

The Separation of the Products

The next step in the procedure was to separate the hydrogen from the other products in order to determine its deuterium content. This was accomplished by letting the products in the reservoir S_2 or S_3 flow slowly through the capillary flowmeter F_1 and then through the trap T_3 filled with silica gel and maintained at $-180°$ C. All the products but hydrogen and some carbon monoxide are removed by this procedure (8). Dry oxygen was metered in at F_2, and the H_2–CO–O_2 mixture was burned on the electrically heated platinum spiral. The resulting water was collected in the cold trap T_4. At the completion of the separation, the water in T_4 was distilled into a bulb attached to the "Outlet" by a ground joint, and was then transferred to a deuterium analysis apparatus.

Deuterium Analysis

The water obtained as above was distilled thoroughly *in vacuo* to remove dissolved carbon dioxide, or other gases, and was then analyzed for its deuterium content by determining the heat conductivity of the saturated vapor at $-21°$ C. as described in previous papers (7, 8).

Materials .

Methyl ether was obtained in cylinders from the Ohio Chemical and Manufacturing Co., and was fractionally distilled before use.

Deutero-acetone was prepared by exchange with deuterium oxide in slightly alkaline solution by the method of Halford, Anderson, Bates, and Swisher (9). Potassium carbonate (0.04 gm.), 99.6% deuterium oxide (10 gm.), and pure acetone (10 gm.) were heated to 43° to 45° C. for about 24 hr. The water and acetone were distilled onto pure anhydrous calcium chloride, and the acetone was rapidly distilled off to a trap kept at $-78°$ C. The calcium chloride was dehydrated by warming to 70° C. and evacuating for about an hour, and the distillation was repeated to remove the remaining traces of water. Analysis showed the product to be 38.8% deuterized. Almost all of this material was used up in trial runs. In preparing a second sample, with which almost all the runs which are reported here were made, light acetone was first "exchanged" with the deuterium oxide residue from the first preparation, and then retreated with 99.6% deuterium oxide. This gave a product which was 48.3% deuterized.

Results

It should be emphasized at the outset that the present work is of a preliminary nature. The experimental technique is difficult since it involves the separation of a small amount of one product from a complex mixture, and its analysis for deuterium on a micro scale. As a result the greatest accuracy to be expected in the deuterium content in the present work is about $\pm 2\%$.

Throughout the present investigation equimolecular mixtures of methyl ether and deutero-acetone were used. Since both molecules contain the same number of hydrogen atoms, complete exchange would yield the following deuterium contents (if it is assumed that the distribution coefficient is unity):

Acetone sample	% D in acetone	% D in hydrogen from the decomposition if exchange were complete
I	38.8	19.4
II	48.3	24.2

However, as discussed above, a free radical mechanism would probably involve as the main steps:

$$HCHO = H + CHO \tag{1}$$
$$CHO = H + CO \tag{2}$$
$$H + CD_3COCD_3 = HD + CD_2COCD_3 \tag{3}$$
$$H + CH_3OCH_3 = H_2 + CH_2OCH_3. \tag{4}$$
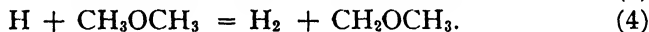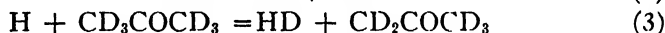
If Reactions (3) and (4) are equally likely, it follows that we would at the most expect the hydrogen to be 25% exchanged, *i.e.*, we would expect the deuterium content of the hydrogen to be 9.7% for acetone Sample I, and 12.1% for Sample II.

It is obviously necessary in the first instance to test the efficiency of the separation of the gases, and to prove the absence of appreciable amounts of hydrogen from the acetone decomposition. This was accomplished by making blank runs in which methyl ether and deutero-acetone were decomposed separately, the products mixed at room temperature, and the hydrogen separated, burned, and analyzed. The results of such runs are given in Table I.

TABLE I

BLANK RUNS TO TEST THE EFFICIENCY OF SEPARATION OF HYDROGEN FROM THE OTHER PRODUCTS. REACTANTS DECOMPOSED SEPARATELY, MIXED, AND THE HYDROGEN SEPARATED, BURNED, AND ANALYZED

Run No.	Acetone sample	% D in hydrogen
2	I	0.0
3	I	1.3
5	II	2.0
6	II	2.0
	Mean	1.3

The mean deuterium content thus found is no greater than that to be expected from the small amount of deuterium formed in the acetone decomposition, and the method of separation of the products may therefore be considered satisfactory.

There is, however, another point which must be tested. Suppose that the two substances decompose entirely independently to give H_2, CH_4, CD_4, C_2D_4, CO, etc. It is still possible that an exchange reaction might occur at the high temperature used, of the type

$$H_2 + CD_4 = HD + CHD_3, \tag{5}$$

or

$$H_2 + C_2D_4 = HD + C_2D_3H \tag{6}$$
$$\text{or} = D_2 + C_2D_2H_2.$$
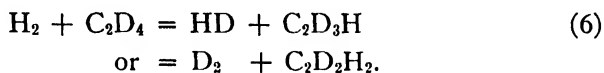
Of these, Reaction 5 is known to be negligibly slow at 590° C. (3, 27). There is, however, considerable likelihood of Reaction (6) occurring via the ethane equilibrium, viz.

$$H_2 + C_2D_4 = C_2D_4H_2 = C_2D_4 + H_2$$
$$\text{or} = C_2D_2H_2 + D_2$$
$$\text{or} = C_2D_3H + HD.$$
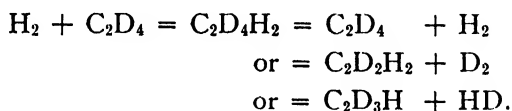
To test this possibility, runs were made in which deutero-acetone and methyl ether were decomposed separately, and the products were then mixed and heated together for a definite time at 590° C. The results of such experiments are given in Table II.

It is apparent from the table that with long periods of heating the exchange reaction becomes troublesome. In fact with 32 min. heating time the exchange has proceeded about halfway to equilibrium. On the other hand, the mean deuterium content of the hydrogen after

TABLE II

BLANK EXPERIMENTS TO TEST THE POSSIBILITY OF AN EXCHANGE REACTION BETWEEN THE PRODUCTS

Run No.	Acetone sample	Heating time, min.	% D in hydrogen
9	II	32	11.8
10	II	5	0.0
12	II	5	6.4
14	II	5	0.0
16	II	5	1.5
18	II	5	6.9
		5	Mean 3.0

five minutes heating time is only 3.0%, as compared with 1.3% for the blank runs given in Table I. Hence, with this time of heating the exchange is not serious. It should, therefore, be safe to draw conclusions from experiments in which mixtures of methyl ether and acetone are heated together at 590° C. for not more than five minutes. It may be mentioned that this time is sufficient to effect the complete decomposition of methyl ether, and to decompose about 90% of the acetone.

The results of experiments with mixtures of the two substances are given in Table III.

A comparison of Tables II and III shows that there is no appreciable increase in the deuterium content of the hydrogen during the decomposition of the mixture. It may therefore be concluded that free hydrogen atoms have not made their appearance to any considerable extent during the process. The results in Tables II and III show considerable fluctuations, which sharply limit the attainable accuracy. The experiments were carried out in pairs, *i.e.*, Runs 10 and 11, 12 and 13, etc., were done in succession and the products analyzed at the same time. It is apparent that the fluctuations usually affected both members of a pair, thus Runs 12, 13, and 18, 19 all gave high results. It is possible that these variations are to be associated with changes in surface activity. It is hoped to obtain more information on this point in further work with improved analytical methods.

TABLE III

DECOMPOSITION OF MIXTURES OF METHYL ETHER AND DEUTERO-ACETONE AT 590° C.

Run No.	Acetone sample	Reaction time, min.	% D in hydrogen
1	I	32	12.8
7	II	32	15.8
8	II	32	11.4
11	II	5	2.0
13	II	5	5.9
15	II	5	2.0
17	II	5	3.9
19	II	5	5.5
		5	Mean 3.9

Discussion

Within the experimental accuracy it may definitely be concluded that there is no noticeable occurrence of the reaction

$$H + CD_3COCD_3 = HD + CD_2COCD_3.$$
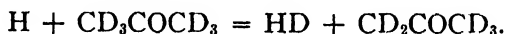
There are obviously two possible causes of the absence of this reaction:

(a) No hydrogen atoms are present during the decomposition process.

(b) Hydrogen atoms are present, but the reaction has too high an activation energy to proceed at a measurable rate. In other words, its activation energy is much higher than those of other hydrogen atom consuming reactions, such as

$$H + HCHO = H_2 + CHO,$$

and

$$H + CH_3OCH_3 = H_2 + CH_2OCH_3.$$
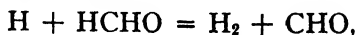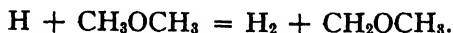
The evidence seems to be definitely against the second explanation. Methyl ether and acetone are molecules of similar complexity, and there is no reason to assume any appreciable difference in the strength of the carbon-hydrogen

bond or in the steric factor (13). Rice (18, 20) assumes the same activation energy for the reactions

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$$

and

$$CH_3 + CH_3OCH_3 = CH_4 + CH_2OCH_3.$$
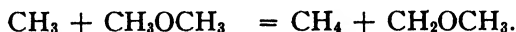
If this is so, there is no reason to expect the hydrogen atom reactions to be very different. As a matter of fact Rice's method of estimating the activation energies of such reactions (20) leads to the conclusion that the reactions of hydrogen atoms with acetone should be faster than the reaction with methyl ether.

It is true that methyl radicals can start a chain decomposition of methyl ether at 400° C., while they cannot do so with acetone (5, 13, 19), and this might be taken as evidence that reactions of the type

$$R + CH_3COCH_3 = RH + CH_2COCH_3$$
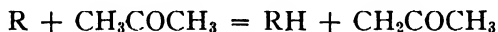
do not occur readily. However, although there is evidence against a chain decomposition of acetone (24, 25, 26), there is also ample evidence that radicals will react with acetone (19). (As a matter of fact there is also some evidence that acetone may decompose by a chain mechanism (1, 12)). It has also been observed (4, 5) that acetone can inhibit the radical sensitized decomposition of acetaldehyde by removing radicals from the system. Hence, while chains are apparently not easy to start in acetone, radicals react with it readily, and there seems to be no reason to doubt that the reaction

$$H + CH_3COCH_3 = H_2 + CH_2COCH_3$$
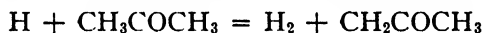
can occur readily at 590° C.

Inasmuch as formaldehyde is present only in small amount, it cannot compete seriously with acetone as a hydrogen atom consuming substance.

We seem therefore to be reduced to the first alternative, *viz.*, that practically no hydrogen atoms are formed in the decomposition processes. This is not in conflict with previous conclusions that radicals may participate in the decomposition of methyl ether (4, 13, 24, 25, 26), since the main steps in the postulated free radical mechanism for the methyl ether decomposition do not involve hydrogen atoms, *viz.*

$$CH_3OCH_3 = CH_3 + CH_3O$$
$$CH_3 + CH_3OCH_3 = CH_4 + CH_2OCH_3$$
$$CH_2OCH_3 = CH_3 + HCHO$$
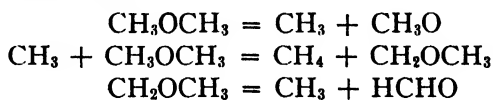
Our results, however, make it very unlikely that formaldehyde can decompose by a free radical mechanism such as

$$HCHO = CHO + H$$
$$CHO = CO + H$$
$$H + HCHO = H_2 + CHO$$
$$2 H = H_2$$
$$2 CHO = HCHO + CO.$$

(with "chain" bracketing the middle three reactions)
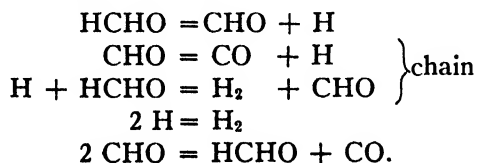
This is in agreement with the conclusions of Patat and Sachsse (15) who found a negligibly small stationary hydrogen atom concentration during the thermal decomposition of formaldehyde.

Fletcher and Rollefson (4) have pointed out that formaldehyde formed as an intermediate in the decomposition of methyl ether itself decomposes about 15 times faster than normal. They suggest that this is due to a sensitized decomposition by methyl radicals from the ether decomposition, *viz.*

$$CH_3 + HCHO = CH_4 + CHO$$
$$CHO = CO + H.$$
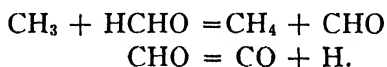
Since this would also involve the occurrence of free hydrogen atoms, our experiments are not in agreement with such a mechanism.

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THE OCCURRENCE OF "MOTTLED ENAMEL" OF TEETH IN ALBERTA AND ITS RELATION TO THE FLUORINE CONTENT OF THE WATER SUPPLY[1]

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Abstract

A partial survey of the Province of Alberta shows that mottled enamel of the teeth in a mild form is endemic in several parts of the province, especially in the area surrounding Lethbridge and in the area south of Red Deer. From an examination of more than 250 samples of water from different parts of the province, a relation has been found to exist between high fluorine in the water supply and the prevalence of mottled enamel.

A great deal of information on the occurrence of the tooth defect known as mottled enamel has been collected since it was described by Black (3) and McKay (15–18). Surveys have shown that it is endemic in many parts of the United States (9), in parts of Europe, Asia, South America, and South Africa. Early investigations proved that the prevalence of this malady was in some way related to the water supply of the region, that the attack on the teeth took place while the permanent teeth were forming, and that the defect persisted throughout the life of the individual. In 1931, Smith, Lantz and Smith (21, 22) produced evidence to prove that mottled enamel is caused by fluorides in the water supply. Churchill (6) arrived at the same conclusion at nearly the same time. Smith and her colleagues were able to show that concentrations of fluorine greater than 1 p.p.m.* induced mottled enamel in young rats, the intensity of the attack increasing with increasing concentrations of fluorine. In regions in which the mottling was endemic the severity of the defect produced on the teeth of humans varied with the fluorine content of the water. As a result of their investigations and those carried out later, it would seem that fluorine is nearly always present in detectable quantities in natural waters, but that at least 1 p.p.m. (17) is necessary to cause the milder form of mottling, which consists of the formation of opaque white spots or bands usually on the upper teeth. The severity of attack and also the depth of color—white, yellow, brown, black—increases as the fluorine content of the water rises to 2 or 4 p.p.m., or more. When the amount present is more than 12 p.p.m. bones are apparently attacked (14).

When the relation between mottled enamel and the fluorine content of water was established, a great deal of interest was shown in the development of methods for determining minute amounts of fluorine. During the last five years many articles on this subject have appeared. Many of the new methods depend upon the fact that zirconium compounds form a red colored lake with sodium alizarinsulphonate, which, in the presence of fluoride, fades in

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*   *p.p.m. = Parts per million parts of water.*

proportion to the amount of fluoride present (5, 8, 16). This reaction leads directly to a colorimetric method. A volumetric method (1, 2, 4, 24) is based on later removing the fluoride from solution by titration with a standard solution of thorium nitrate; in this way the lake is allowed to form. Others (10, 11, 12, 23) make use of the fact that fluorides when added to a known amount of ferric ion produce the ferri-fluoride ion, FeF_6^{-3}, so that when thiocyanate is added, the color formed is due to the excess of ferric ion. The spectrograph (6) has also been used. Much of the work in perfecting methods of analysis has been done because of the tendency of other ions to interfere, so that modifications have had to be made. One might say that at the present time methods of determining small amounts of fluorine are fairly satisfactory, although the different methods do give slightly different results.

In the discussions on mottled enamel which appear in the various scientific journals there is no mention of its occurrence in Canada. It is the purpose of this paper to present evidence that there are, in Alberta, several 'districts where the teeth of many of the children show marked signs of mottling, but, in most cases, of the opaque white, or mild, variety, although several sets of teeth have been examined on which the spots were yellow or light brown. The first evidence came in July, 1935, from Granum in Southern Alberta when the principal of the school described to one of the writers the peculiar appearance of the teeth of some of the children. It was suggested that the trouble was mottled enamel. Clinical evidence from the local dentist was requested and arrangements were made to obtain samples of water from wells in the district. Later, it was learned that the Provincial Travelling Clinic had observed 14 cases at its Grassy Lake centre, the children coming from three different schools. Samples of water were requested from families in these districts. When the University session opened, students coming from several other districts were noticed who had mottled enamel.

Because of these facts, a survey was begun in which as much data as possible were collected and, at the same time, samples of water from many points were obtained and analyzed for fluorine content. Questionnaires were sent to dentists and doctors in the affected areas and co-operation was obtained from the Provincial Department of Health. Students were asked to bring in samples of water, and to report as much evidence of teeth disfigurement as possible. Samples of water received by the Provincial Analyst from different parts of the province were also examined for fluorine content. The teeth of all new students entering the University in the fall of 1936 were examined for this defect by a dentist.

The information received on the prevalence of mottled enamel is not nearly as complete as had been expected. Efforts have been made to obtain as complete a case history of the people as possible, and only those have been included who have lived in the one district between the ages of two and twelve years. It has been rather difficult to ascertain when a family has abandoned one well and begun to use another, and the water supply in many districts comes from both deep and shallow wells in which fluorine content varies

over a wide range. Another difficulty that has been encountered in the survey is,the sparseness of settlement and the scarcity of dentists. In addition, the mottled enamel is, of itself, not always sufficient cause for a visit to the dentist.

As the methods for the determination of minute quantities of fluorine are all very recent, it was found necessary to check up on a number of them in order to select the ones that best suited the conditions, and to modify them wherever necessary. After a considerable amount of work had been done it was decided to use; *(a)* a modification of Sanchis' method (19) for amounts of fluorine between 0 and 0.75 p.p.m.; *(b)* Sanchis' regular method for amounts between 0.75 and 3 p.p.m.; and *(c)* a revision of Armstrong's modification (1) of Boruff and Abbot's distillation method (4), which is based on the macro method of Willard and Winter (24), for amounts greater than 2 p.p.m.

In all cases the Sanchis method and the modified Sanchis method were first used, and if the sample contained more than 2 p.p.m. of fluorine, the modified method of Armstrong was used and thus an overlapping was obtained. The first two methods are colorimetric in character and require 100 cc. of water, while the last method is titrimetric, the amount of water required depending on the concentration of fluorine in the water.

Details of the Sanchis method will be found in the original article. It consists essentially of forming the red lake of sodium alizarinsulphonate or alizarin red with a zirconium salt. The color changes on addition of fluoride progressively to a yellow due to the formation of one of the zirconium fluoride (13) complexes, $Zr_3F_{17}^{-5}$, $Zr_2F_{13}^{-5}$, ZrF_5^{-1}, ZrF_6^{-2} or ZrF_7^{-3}, which causes the decomposition of the lake. The reactions are carried out in the presence of large excess of hydrochloric and sulphuric acids to minimize the effect of interfering anions in the natural waters. The colors developed in the solutions containing fluorides were compared with those of standards made up from definite amounts of fluorine, as sodium fluoride, treated in the same manner.

In the modified Sanchis method, to 100 cc. of the water were added 2.0 cc. of 3 N hydrochloric acid, 2.0 cc. of 3 N sulphuric acid and 1.75 cc. of the indicator containing 0.17 mg. of sodium alizarinsulphonate and 0.87 mg. of c.p. zirconium nitrate, $ZrO(NO_3)_2 . 2H_2O$, per cc. The solution was heated to boiling, allowed to stand for four hours, transferred to a Nessler tube, and the color was matched with solutions containing known amounts of sodium fluoride treated in the same manner.

For the modified Armstrong method the amount of water used was such that approximately 0.2 mg. of fluorine was present. This was made alkaline to phenolphthalein with 0.2 N sodium hydroxide and concentrated to 50 cc. This was then placed in a 250 cc. distilling flask along with 20 cc. of concentrated sulphuric acid and some glass beads. The flask was fitted with a thermometer extending into the liquid and a dropping funnel connected to a capillary tube also extending into the liquid so that water could be added from time to time. Water was added so that distillation started at 110° C.,

and distillation was continued until 75–100 cc. of distillate was collected. Water was added through the funnel so that the temperature rose no higher than 135° C. By this method practically all interfering ions were separated. The distillate was made alkaline to phenolphthalein, concentrated to 20 cc., transferred to a 250 cc. Erlenmeyer flask along with 20 cc. of 95% ethyl alcohol and six drops of indicator, which is a 0.5% solution of sodium alizarin-sulphonate. Armstrong used only three drops but the writers obtained better results with the larger quantity. The contents of the flask was decolorized with 0.2 N hydrochloric acid, one drop being added in excess. This was then titrated to a faint permanent pink with standard thorium nitrate solution from a 10 cc. microburette. After subtracting the blank required for the formation of the thorium lake, which amounted to 0.03 cc., the parts per million of fluorine in the water were calculated. The thorium nitrate solution, the concentration of which was between 0.01 N and 0.02 N, was standardized against a 0.02 N solution of sodium fluoride. There is a remarkable similarity between this modified method and the method reported in Armstrong's most recent paper (2).

The colorimetric methods are more convenient than the titration method as more samples can be run at one time and smaller amounts of water are required. The titration method, however, can be used for colored waters where the colorimetric method is unsatisfactory owing to the masking of the end point, and for waters where such interfering substances as sulphate or phosphate ions are present in large quantities.

Information on mottled enamel so far collected in the province indicates that there are several districts in which the tooth defect is fairly widespread. As a general rule the attack on the teeth is slight, the mottling consisting of white opaque spots on the upper teeth, although several cases have been observed in which yellow patches were noticed.

Fig. 1 is a map of the southern half of the province of Alberta. There are apparently two areas in the province where mottled enamel of the teeth has been observed, one in the vicinity of Lethbridge and the other in the vicinity of Red Deer. The malady is not endemic in all districts of each of these areas, but it would seem that some districts are free from this tooth defect.

In the Lethbridge area the mottling is most prevalent in and around Claresholm (B) and Granum (C). (Letters refer to Fig. 1.) The water supply comes from deep wells, and in those which have been examined fluorine content is high. Unaffected children in these districts obtained their drinking water from other wells which are shallow and contain less than 1 p.p.m. of fluorine. A mild type of mottled enamel is found at Cardston (F) and in its vicinity. In this district mottling of the teeth of animals has been observed. The water supply in this district consists of creeks, sloughs, and deep wells. Those who use creek water in the town exhibit mottling, but samples of water from this source taken in the winter and early spring show low fluorine content. It may be that the creek obtains part of its supply in the summer from mountain springs which do not flow in the winter, and
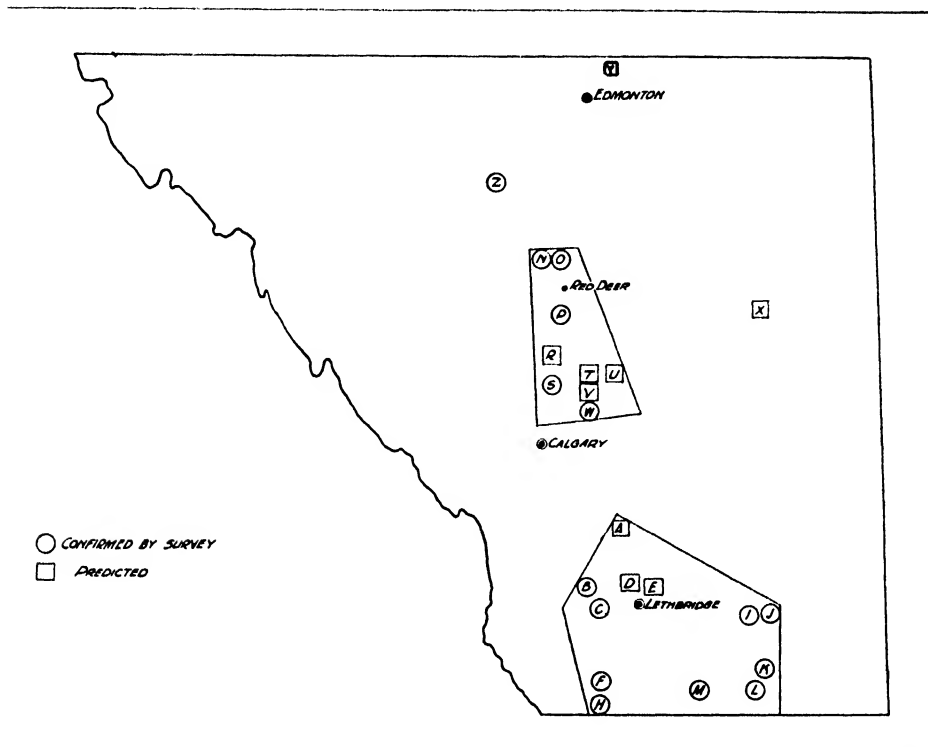
FIG. 1. *Areas in Alberta in which mottled enamel of the teeth has been observed.*

thus the water varies in fluorine content. Arrangements were made to obtain monthly samples during the summer, but the samples were lost or the bottles were broken in the mail. Mottling of the teeth also occurs 15 miles south at Kimball (H). A number of cases have been reported from Foremost (K), Grassy Lake (I), Burdett (J), and Lucky Strike (L). Water was received from all these points. Confirmation of the relation between mottled enamel and high fluorine content was obtained from the first three points. Affected people use water from deep wells. However, the water from a deep well at Lucky Strike is quite low in fluorine. Most of the cases in this district are users of water from shallow wells from which samples have not yet been obtained. Undoubtedly, as more information is received, the affected part of this area will be increased. One case has been reported from Milk River (M), but no water from this place has been examined. From the fluorine content of waters from other points it is predicted that cases of mottling will be found at Vulcan (A), Barons (D), and Picture Butte (E).

Reports on the Red Deer area are not so numerous as in the more southern area. Clinical evidence of cases from Innisfail (P), Didsbury (S), Beiseker (W) Bentley (N), and Blackfalds (O) have been obtained, and a relation was found to exist between mottled enamel and high fluorine content. It is expected that cases of mottled enamel will be found at Three Hills (U), Olds (R),

Acme (V), and Allingham (T). The deep wells in this area are mostly high in fluorine content, while the shallow wells are low in fluorine.

Mottled enamel also occurs west of Wetaskiwin (Z), but at the present time nothing is known of the character of water used in the district. Information just obtained indicates a number of mild cases near Tawatinaw (Y). Single cases of mottling have been reported from Calgary, Wabamum, and Fawcett, but the water supplies from all three were low in fluorine. A number of other parts of the province may be affected but such information is not available. From water analyses it is expected that there will be some cases near Coronation (X) and Viking.

In this water survey 254 samples have been analyzed. The fluorine contents are shown in Table I. Depths of wells are given. For convenience, the province has been divided into five parts; (a) the Peace River area,

TABLE I

Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.	Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.
(a) Peace River Area							
31	Bad Heart	—	0.0	109	Peace River	28	0.85
87	Chinook Valley	12	0.5	42	Valhalla Centre	37	0.1
217	Grimshaw	42	0.4	43	Valhalla Centre	110	0.5
18	Peace River	—	0.1	106	Wanham	8	0.4
71	Peace River	48	0.2	91	Whitelaw	40	1.1
(b) Central Alberta Area							
60	Alcomdale	22	0.2	58	Edson	—	0.0
54	Alliance	—	0.35	211	Elbridge	22	0.4
103	Andrew	35	0.3	159	Elk Island Park	—	0.75
104	Andrew	30	0.3	150	Elk Point	15	0.5
120	Andrew	30	0.3	59	Evansburg	—	0.05
251	Ardrossan	148	0.15	28	Fawcett	—	0.25
77	Athabasca	24	0.2	137	Fawcett	15	0.3
240	Berrymoor	50	0.05	189	Gratz	42	0.2
116	Beverly	—	0.2	84	Hairy Hill	60	0.1
250	Blackfoot	208	0.3	145	Hardisty	—	0.1
158	Botha	35	0.5	30	Hayter	—	0.2
152	Busby	31	0.8	238	Heath	50	0.05
221	Carvel	—	1.1	202	Heath	410	0.4
209	Cousins	Slough	0.7	220	Heath	40	0.35
252	Cherhill	26	0.3	160	Hobbema	250	1.1
204	Clandonald	—	0.4	117	Holden	8	0.1
176	Cold Lake	60	0.3	231	Inland	225	0.35
142	Condor	—	0.1	83	Hughenden	238	0.25
99	Cooking Lake	25	0.3	230	Innisfree	68	0.15
181	Cooking Lake	—	0.2	213	Jasper	Lake	0.05
143	Daysland	—	0.3	244	Kingman	144	0.25
232	Derwent	65	0.35	12	Kitscoty	42	0.6
180	Dewberry	70	0.7	92	Kitscoty	30	0.3
194	Dewberry	300	0.4	124	Kitscoty	28	0.4
49	Donalda	Spring 10'	0.6	107	Lacombe	110	0.05
				88	Legal	61	0.0
183	Duhamel	84	0.1	203	Legal	325	1.3
121	Edgerton	35	0.1	212	Legoff	18	0.5
37	Edmonton	40	0.1	23	Lloydminster	140	0.1
226	Edmonton	River	0.05	144	Lougheed	—	0.5

TABLE I—*Continued*

Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.	Sample No.	Place	Depth of well, ft.	Fluorine, p.p.m.
(b) Central Alberta Area—concluded							
125	Mannville	—	0.05	3	Stettler	—	0.5
234	Marwayne	59	0.0	12	Stettler	250	0.9
7	Millet	80	0.6	61	Stettler	30	1.1
237	Mirror	175	0.6	113	South Cooking Lake	54	0.5
151	Myrnam	38	0.75	246	Springfield	8	0.35
178	Myrnam	40	0.1	24	Stony Plain	—	0.4
179	Myrnam	50	0.05	161	Tawatinaw	Stream	0.4
229	Nevis	90	0.5	119	Thorsby	—	0.6
218	Nisku	220	1.2	25	Tofield	—	0.2
140	Nordegg	River	0.2	192	Tofield	—	0.6
235	North Bank	—	0.3	130	Vegreville	22	0.3
79	Pibroch	104	0.0	4	Vermilion	140	0.1
164	Plamonden	20	0.7	68	Vermilion	125	0.05
105	Radway	—	0.0	9	Viking	206	1.0
233	Ranfurly	60	0.3	10	Viking	90	1.2
118	Rivercourse	23	0.3	50	Villeneuve	52	0.05
82	Rochfort Bridge	—	0.25	96	Wabamun	—	0.25
208	Ryley	293	0.5	165	Wainwright	—	0.25
51	Sedgwick	125	0.05	5	Westlock	125	0.8
157	Slave Lake	14	0.2	6	Westlock	Spring	0.5
1	Smoky Lake	—	0.2	219	Willingdon	38	0.8
57	Smoky Lake	—	0.3	207	Winterburn	32	0.35
2	Stettler	70	0.5				
(c) Red Deer Area (Endemic)							
98	Allingham	167	1.0	102	Olds	26	0.25
35	Acme	125	0.5	155	Olds	241	2.3
36	Acme	157	2.2	163	Olds	32	2.0
78	Bentley	60	3.0	205	Olds	157	0 3
170	Bentley	95	0.5	187	Penhold	90	0.4
171	Bentley	90	1.0	76	Red Deer	River	0.1
172	Bentley	108	0.5	182	Red Deer	40	0.1
11	Didsbury	180	1.3	248	Sunny Slope	80	0.15
154	Didsbury	45	0.7	26	Swalwell	—	0.5
199	Grainger	242	0.4	85	Three Hills	374	2.3
253	Innisfail	—	0.6	173	Three Hills	380	2.3
133	Innisfail	156	2.9	174	Three Hills	265	1.5
254	Innisfail	—	0.2	175	Three Hills	30	0.4
184	Innisfail	130	0.3	201	Three Hills	500	3.1
216	Kathryn	205	1.3				
(d) Southern Alberta Area							
32	Ardenode	—	0.4	97	Calgary	150	0.25
249	Arrowwood	74	0.3	200	Calgary	25	0.25
69	Baintree	111	0.2	67	Carbon	171	0.1
64	Banff	Cave and basin	0.9	162	Carbon	8	0.3
				80	Cochrane	45	0.0
65	Banff	River	0.1	215	Consort	187	1.2
197	Beynon	26	1.0	34	Coronation	100	1.3
223	Beynon	24	1.0	135	Coronation	180	0.5
132	Big Valley	42	0.6	136	Coronation	247	0.7
112	Blairmore	River	0.05	56	Delburne	—	0.05
33	Bottrell	—	0.1	153	Delburne	30	0.3
241	Byemoor	135	0.05	52	Drumheller	60	0.0
21	Calgary	River	0.3	110	Drumheller	River	0.1
46	Calgary	River	0.3	39	Elkton	40	0.0
62	Calgary	90	0.05	40	Elkton	60	0.2

TABLE I—*Concluded*

Sample No.	Place	Depth of well. ft.	Fluorine. p.p.m.	Sample No.	Place	Depth of well. ft	Fluorine, p.p.m.

(d) Southern Alberta Area—concluded

Sample No.	Place	Depth of well. ft.	Fluorine. p.p.m.	Sample No.	Place	Depth of well. ft	Fluorine, p.p.m.
222	Ensign	75	0.6	188	Okotoks	14	0.1
177	Gleichen	—	1.0	90	Pincher Creek	11	1.0
236	Ghost Pine Creek	200	1.2	128	Redcliffe	30	0.0
47	Hanna	140	0.5	13	Shepard	30	1.4
131	Hanna	114	0.03	243	Stanmore	200	0.6
129	Hartell	22	0.7	206	Strathmore	75	0.2
225	High River	150	1.4	149	Throne	180	1.4
214	Hill Spring	Spring	0.8	44	Trochu	125	0.25
239	Hubalta	280	1.7	66	Trochu	110	0.3
55	Irvine	—	0.6	70	Turner Valley	Creek	0.2
191	Lundbreck	18	0 2	210	Turner Valley	Creek	0.3
245	Manyberries	640	>1.0	100	Walsh	Spring	0.1
41	Medicine Hat	River	0.2	95	Wayne	14	0.2
198	Milo	30	0.6	190	West Wingham	40	0.1
247	Milo	185	0.5	8	Whitla	20	0.8
29	Okotoks	—	0.15	123	Winnifred	780	0.5
127	Okotoks	Creek	0.5	45	Youngstown	17	0.4

(e) Lethbridge Area (Endemic)

Sample No.	Place	Depth of well. ft.	Fluorine. p.p.m.	Sample No.	Place	Depth of well. ft	Fluorine, p.p.m.
108	Barons	8	0.7	169	Granum	62	3.0
156	Barons	10	1.1	185	Granum	80	2.4
227	Barons	90	0.7	186	Granum	80	0.6
48	Burdett	630	2.7	166	Grassy Lake	450	3 0
138	Burdett	40	0.4	141	Kimball	190	2.2
139	Burdett	600	1.1	134	Lucky Strike	1383	0.3
15	Cardston	Creek	0.0	89	Macleod	23	0.1
16	Cardston	124	0.1	93	Macleod	24	0 1
114	Cardston	Creek	0.1	94	Macleod	24	0.1
195	Cardston	Creek	0.25	224	Monarch	—	0.6
196	Cardston	80	0.1	193	New Dayton	6	1.2
242	Cardston	40	0.35	81	Picture Butte	Spring	1.0
19	Claresholm	98	4.15	101	Picture Butte	Spring	0.0
20	Claresholm	130	3.85	147	Picture Butte	Reser-	0.5
53	Claresholm	128	4.6			voir	
122	Claresholm	—	0.5	148	Picture Butte	—	1.4
146	Coutts	400	0.7	115	Purple Springs	15	0.7
167	Coutts	115	0.0	27	Raymond	145	1.2
73	Foremost	640	1 4	74	Raymond	42	0.1
63	Granum	90	2.45	86	Taber	Spring	0.5
111	Granum	28	0	75	Vulcan	220	2.6
126	Granum	106	2.2	228	Vulcan	80	1.4
168	Granum	120	2 0				

(b) Central area, *(c)* the Red Deer endemic area, *(d)* the Southern area, and *(e)* the Lethbridge endemic area. Fig. 2 is a map of the Province of Alberta showing the location of the wells examined, and marked according to depth and fluorine content. Deep wells are those more than 80 ft. in depth. Streams and springs are included with the shallow wells. It will be seen that many districts in the southern half of the province have contributed samples, but most of the sparsely populated sections have not been examined. It will be seen that, in general, in the endemic areas the deep wells are high in fluorine.

There are, however, a number of shallow wells in the Lethbridge area that contain more than 1 p.p.m. of fluorine. These wells are either springs or are supplied by seepage from irrigation ditches.
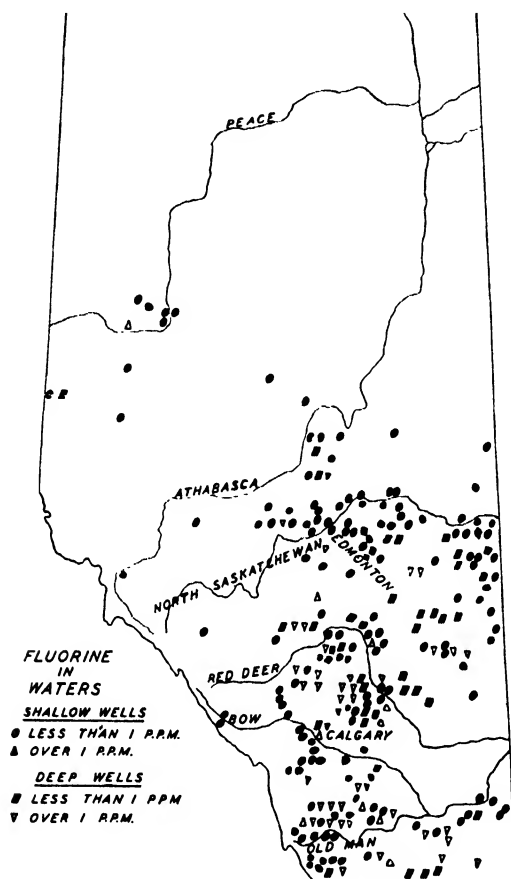
FIG. 2.   Map of Alberta showing location of the wells examined.

No attempt has yet been made to find the source of the fluorine in the water, nor to locate the geological strata through which the waters pass.

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WATER SOLUBLE ACID SUBSTANCES IN THE RAW HUMUS OF PODSOL SOILS[1]

By H. R. Sallans[2], J. M. Snell[2], H. W. Mackinney[2], and R. R. McKibbin[3]

Abstract

Aqueous extracts of "raw humus" from a typical Quebec podsol soil have been studied by means of two methods of fractionation. The presence of free acetic acid and mannitol has been established, and evidence of the presence of formic acid has been obtained. Data are presented which show that a number of organic acids are present in small quantities.

The most prevalent virgin soil type found in the province of Quebec is the podsol. Surface waters percolating through the soil have removed soluble bases from the upper soil horizons and brought about a deposition of sesquioxide-organic complexes at lower levels. A knowledge of the causes of this leaching process may suggest means of increasing the fertility of podsolized soils.

Laboratory experiments have shown that aqueous extracts of the surface layer of decaying organic matter are strongly acid in reaction and exert a leaching effect on the subsoil. An examination of these extracts was undertaken to determine the nature of the substances present. Particular attention was given to acid substances since they are known to cause leaching of soil minerals (5).

Though much attention has been given to the hydrogen ion concentration of soils, little information has been obtained regarding the nature of the acids present. The mineral acids, sulphuric and phosphoric, are considered by some workers (1) to be responsible for soil acidity, but this hypothesis has not been proved. Schreiner and Shorey (8, 9, 10) and Shorey (11, 12) have isolated a number of organic acids from soils. However, the methods used for the isolations and the nature of the soils investigated make it appear highly improbable that these acids occurred in the free state.

The material used for the present investigation was "raw humus" from a typical sandy podsol near Ste. Anne de Bellevue, Quebec. The humus was obtained from an almost pure stand of hemlock (*Tsuga canadensis*), was

strongly acid in reaction, and contained 16 to 20% of ash. Extracts were prepared and subjected to an examination by two methods, one based on precipitation with barium hydroxide and the other on a preliminary fractionation with organic solvents.

Two organic substances were isolated from the extracts. Mannitol was obtained in amounts representing 3 to 4% of the dissolved organic matter. The baryta method yielded acetic acid in an amount equivalent to about 8% of the total acidity, and evidence was obtained of the presence of formic acid in about one-fourth of this amount. The method of solvent fractionation also gave evidence of the presence of volatile acids in an equivalent amount, and since in this case the acids were distilled under reduced pressure directly from the extracts it is concluded that they were present in the free state.

As far as the authors are aware, the presence of free acetic and formic acids in soils of this type has not been reported previously. Mannitol was found in soil by Shorey (11). Raistrick and co-workers (2) found it as an intermediate product in the action of molds on glucose. While the source of the mannitol is not definitely known, its presence appears significant because polyhydroxy compounds form complexes with trivalent bases.

Experimental

Preparation of Soil Extracts

The humus was screened and saturated with distilled water in four-litre percolators holding 700 grams of humus each, allowed to stand for 20 hr., drained, and washed with 0.5 litres of water, and the process repeated once. The extracts varied slightly in composition but the following data are typical. From 1000 gm. of anhydrous humus 4.3 litres of extract, containing 3.5 gm. of dry matter, was collected.   The pH of the solution was 3.3, and the total acidity was equivalent to about 5.2 ml. of normal acid.

The extracts were colored and highly buffered. Consequently the acid values were determined electrometrically by means of a hydrogen electrode. Titration curves were drawn and the equivalence point was taken as pH 7.0.

Fractionation by Means of Barium Salts

The filtered extract was treated with a slight excess of saturated barium hydroxide solution. A dark brown precipitate containing the insoluble barium salts was filtered off and washed with hot water. This precipitate was treated with the calculated amount of sulphuric acid, and the liberated acids were divided into water soluble and water insoluble fractions. The insoluble acids were separated from barium sulphate with sodium carbonate. The distribution of the acidity for these fractions is given in Table I. The combined filtrate and washings containing the soluble barium salts were treated with carbon dioxide and concentrated at 80° C. The acids were liberated with sulphuric acid and distilled. Data for the acidity of the volatile and non-volatile fractions are given in Table I.

TABLE I

DISTRIBUTION OF ACIDITY IN EXTRACTS BY THE BARYTA METHOD OF FRACTIONATION

Fraction	0.1 N acid per kg. of humus, ml.	Total acidity, %
Barium salts insoluble in water		
Acids soluble in water	22.0	29.4
Acids insoluble in water	1.9	2.5
Barium salts soluble in water		
Volatile acids	12.8	17.1
Non-volatile acids	29.0	38.6
Recovery	65.7	87.6

A quantity of the distillate equivalent to 30 kg. of humus was made slightly alkaline and concentrated to a volume of 10 ml. After acidification with sulphuric acid the solution was extracted with ether. Two fractionations of the ethereal solution yielded 2 ml. of a fraction boiling at 100° to 110° C., which exhibited a reducing effect on Tollens' solution. Formic acid was determined in one-half of this fraction by a modification of Scala's method (4, 7, 13), in which the mercurous chloride was weighed. Found: HCOOH, 0.012 gm. per kg. of raw humus, which is equivalent to 21% of the volatile acidity.

The remainder of this fraction was treated with p-phenylphenacyl bromide (3) and after two recrystallizations the resulting ester was found to have a melting point of 109° C. No depression of the melting point occurred when this ester was mixed with an authentic specimen of p-phenylphenacyl acetate, m.p. 110° C. About one-fifth of the volatile acidity is, therefore, due to formic acid, and the remainder largely to acetic acid.

The residue that remained after removal of the volatile fraction was dissolved in a minimum quantity of water, treated with five volumes of 95% ethyl alcohol, and filtered to remove precipitated gums. The filtrate, when treated with two-thirds its volume of ether, yielded mannitol. The mannitol was recrystallized from alcohol and its identity was confirmed by the melting point when admixed with an authentic specimen.

This fraction contained, besides mannitol, a mixture of distinctly acid substances which were neither colloidal nor resinous, but all attempts to isolate individual acids were unsuccessful.

Fractionation by Means of Solvents

After a number of preliminary investigations the scheme of fractionation outlined in Fig. 1 was developed. Analyses of the various fractions are given in Table II.

Aqueous extract
|
Concentrated *in vacuo*

70% ethanol

Volatile fraction

Fraction I
insoluble

96% ethanol

Fraction II
insoluble

100% ethanol

Ethanol removed

Fraction III
mannitol

Acetone

Insoluble

Acetone removed

100% ethanol

Aqueous solution

Butanol

Fraction VI
insoluble

Fraction VII
soluble

Fraction IV
butanol
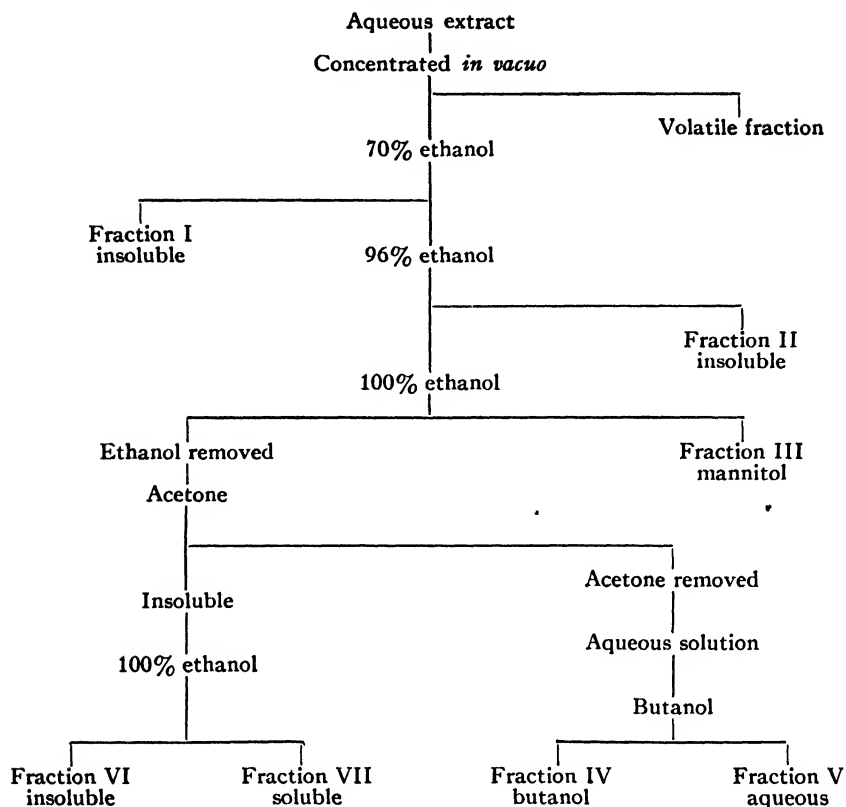
Fraction V
aqueous

FIG. 1.   *Fractionation of humus extracts by means of solvents.*

TABLE II

ANALYSES OF FRACTIONS OBTAINED FROM HUMUS EXTRACTS BY MEANS OF SOLVENTS

Fraction	Relative leaching power*	Solids, %	Acidity, %	Acid equivalent	Nitrogen, %	Sulphur, %	Phosphorus, %
Volatile	38	1.1	11.5	60	0.0	0.0	0.0
Insoluble in ethanol							
I. 70%	—	26.6	24.0	780			
II. 96%	131	26.1	10.6	1650	3.2	6.3	0.3
Soluble in acetone							
IV. Sol. butanol	166	8.9	25.9	230	0.0	0.0	0.0
V. Sol. water	389	3.1	8.6	245	0.0	0.0	0.0
Insoluble in acetone							
VI. Insol. ethanol	—	3.4	0.0	0.0	—	—	—
VII. Sol. ethanol	194	4.3	13.8	208	2.4	2.7	0.01

Milligrams of iron removed from 2.0 gm. of soil by 0.5 gm. of each fraction in 100 ml. of water.

In a typical experiment, the filtered extract from 25 kg. of anhydrous raw humus (94 litres, containing 76.2 gm. of dissolved solids) was concentrated to two litres, in an atmosphere of nitrogen, under reduced pressure below 40° C., and filtered. The filtrate was poured in a fine stream, with agitation, into seven litres of 95% ethanol; thus the concentration of the ethanol was reduced to 70%. The precipitate was washed first with 70% ethanol, then with 95% ethanol and dried over sulphuric acid and solid sodium hydroxide under reduced pressure. It was a brown powder weighing 20.3 gm. (26.6% of the total dissolved solids). The filtrate and washings, concentrated to 100 ml. and poured into absolute ethanol to a final concentration of 97%, yielded a further precipitate of 21.5 gm. (28.2% of the dissolved solids.) In a similar experiment in which 17 kg. of raw humus was used the two alcohol precipitated products amounted, respectively, to 26.5 and 23.9% of the dissolved solids.

The red alcoholic filtrate, concentrated to less than 100 ml. and treated with additional absolute ethanol, deposited crystals, which, after recrystallization from 90% ethanol, were identified as mannitol by the method of mixed melting points and also by the preparation of the hexacetate, m.p. 120° C. The quantity isolated constituted 3 to 4% of the total organic matter of the soil extract.

The volatile acids were collected during concentration of the extracts. Qualitative tests indicated the presence of acetic acid, but attempts to prepare the *p*-phenylphenacyl ester yielded a mixture of derivatives which could not be separated by fractional crystallization.

Fraction IV was dissolved in dry methanol and treated at 2° C. with 9.0 gm. of diazomethane generated by the method of Meerwein and Burneleit (6). The esters were extracted from an aqueous medium with ether, freed from acid material with 2.5% potassium carbonate solution and fractionally distilled. The following fractions were obtained.

(a) B.p. 40° to 50° C. at 25 mm. 0.12 gm. of colorless mobile liquid. Redistilled, b.p. 89° to 89.5° C. at 760 mm., 0.08 gm.

(b) B.p. 60° to 65° C. at 0.5 to 0.6 mm., 0.15 gm. of yellow oil.

(c) B.p. 97° to 100° C. at 0.1 mm., 0.20 gm. of yellow oil.

(d) B.p. 140° to 160° C. at 0.04 mm., 0.40 gm. of resinous yellow oil. Redistilled, b.p. 120° to 122° C. at 0.03 mm., 0.30 gm. of yellow oil with tendency to crystallize on standing.

The esters were obtained in quantities too small for identification. The *p*-phenylphenacyl ester was prepared from Fraction *(a)*, and it melted at 120° C. A search of the literature failed to identify this derivative.

Fraction VII was dissolved in water and an aliquot was treated with barium hydroxide. A colloidal precipitate formed which was free from sulphur and was completely soluble in dilute hydrochloric acid. It is, therefore, evident that the acidity of this fraction was not due to sulphuric acid. Picric acid

yielded a mixture of crystalline picrates which could not be separated, owing to the small quantity of material available and the presence of colloidal impurities. The excess picric acid was removed and the solution treated with phosphotungstic acid. A white precipitate containing sulphur but no nitrogen was obtained. As the picrates were sulphur-free and contained all the nitrogen of the extract, a complete separation of sulphur and nitrogen had been realized.

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THE 3,4-DIPHENYLCHLOROCYCLOPENTENONES AND RELATED COMPOUNDS[1]

By C. F. H. Allen[2] and H. Rudoff[3]

Abstract

The uncertainties as to structures in the 3, 4–diphenylchlorocyclopentenones have been cleared up by the synthesis of all four possible isomers and a study of their reactions. The investigation of the related indones has been continued, and an interpretation of new evidence is suggested.

In order to clear up the uncertainties as to the location of the double bond and of the chlorine atom in the diphenylcyclopentenone series, the earlier work (3) has been extended and evidence secured which makes it possible to assign definite structures to each form. The four possible isomers are represented by Formulas I to IV.

I   II   III   IV
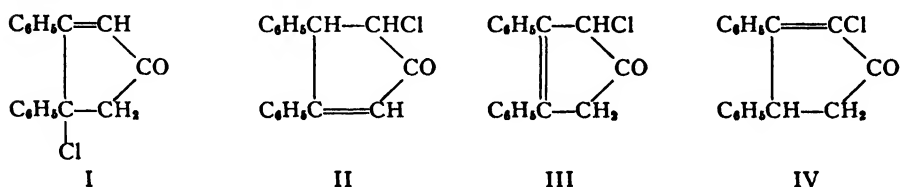
A substance corresponding to I was first made and its structure determined in this laboratory (3); this formula was confirmed and accepted by other workers in the field (7). At the same time (3) the arrangement shown in II was assigned to an isomeric chloride, first obtained 50 years ago by Japp (12), because both gave the same indone by loss of hydrogen chloride on treatment with alkaline reagents. This structure, however, was not accepted by the English investigators (7) who preferred to represent it as IV for reasons that seemed best to them. They also synthesized a third chloride, to which was assigned Formula III, and with which the writers are in agreement.

To complete the series and end the confusion, the writers have synthesized the fourth possible isomer; so now all are known and it remains only to assign structures to the new one and to Japp's. All four contain the cyclopentenone system, for each can be converted into the diphenylcyclopentenone V. Each gives a different dinitrophenylhydrazone when treated with 2,4–dinitrophenylhydrazine. This not only serves as a means of identification but also shows that each contains a carbonyl group.
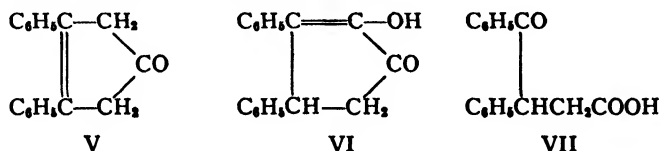
V   VI   VII

The fourth chloride was prepared by the action of phosphoryl or sulphuryl chloride on Vorländer's ketol, VI. This type of reaction was employed by Emil Fischer in his work with the purines, to replace the hydroxyl group on a doubly bound carbon by a chlorine atom (11). When the new chloride was ozonized a 60% yield of desylacetic acid, VII, resulted; thus the double bond was located. This reaction, taken in conjunction with the method of preparation, and the inactivity of the chlorine, makes certain Structure IV for the new isomer. By exclusion, therefore, Japp's isomer must be represented by II as the writers formerly postulated, though the reason given at that time is no longer valid.*

The conversion of chloride I to II, described in the earlier paper, is, as the English investigators suggested, a case of anionotropy, for it is brought about by hydrogen chloride or hydrogen bromide in acetic acid; if it were elimination and addition, a bromide should have resulted in the second case. The sequence of shifts, *i.e.*, whether chlorine or hydrogen migrates first, is uncertain; a prior movement of chlorine would give III, but since attempts to rearrange III to II in the same way were unsuccessful, such an assumption seems unwarranted.

The difference in reactivity of the chlorine atom in these compounds makes it possible to put them into two groups. The first, which give immediate precipitates with silver nitrate, contains I and III, the chlorine of the former resembling that of a tertiary chloride such as triphenylchloromethane, while both are like allyl chloride. The second group contains II and IV; the chlorine atom is relatively inactive and gives no precipitate with silver nitrate.

Though each chloride gives a dinitrophenylhydrazone, the derivative from III has lost its chlorine; it is monomolecular and believed to be the dinitrophenylhydrazone of diphenylcyclopentadienone, VIII. It could not be split into its components; all the variations ever reported (1) for cleavage of dinitrophenylhydrazones were tried, but the derivative was recovered unchanged. An alternative, Formula IX, containing a four-membered ring is possible but extremely improbable.

$$C_6H_5C = CH$$
$$C = NNHC_6H_3(NO_2)_2$$
$$C_6H_5C = CH$$
VIII

$$C_6H_5C = C\text{------}NC_6H_3(NO_2)_2$$
$$C = N$$
$$C_6H_5C = CH$$
IX
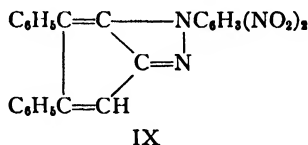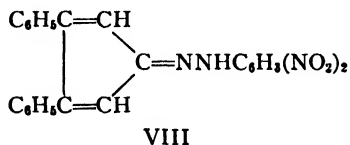
All the chlorides react with basic reagents, but the products are not always well defined. Chloride I loses hydrogen chloride the most easily, any basic reagent (even silver nitrate) causing the formation of the indone X (3). The latter is also secured from II but only by the use of a strong base such as sodium hydroxide. Isomer III gives with sodium hydroxide a monochlorin-

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*Burton, Shoppee and Wilson (7) obtained some desylacetic acid by the permanganate oxidation of Japp's chloride. This led them to advocate IV for this substance; ozonolysis yielded an oil. Since the use of alkaline reagents, such as permanganate, is not trustworthy in $\alpha,\beta - \beta,\gamma$-unsaturated systems in which shifts of hydrogen and double bonds are possible, this reaction cannot be considered reliable for proving structure.

done XI, which on boiling with sodium methylate loses hydrogen chloride to give X. It is thus to be represented as a hydrogen chloride addition product of X rather than as a substitution product which the English investigators suggested, based on their method of preparation.

$$
\begin{array}{cc}
\text{X} & \text{XI}
\end{array}
$$
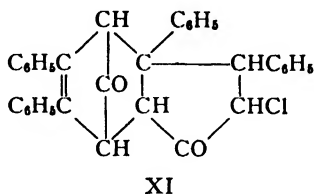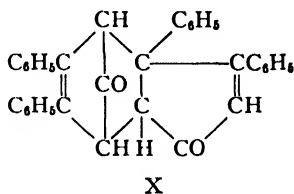
Chloride IV likewise loses hydrogen chloride, when sodium carbonate and dilute alcohol are used; the product is bimolecular, but its exact nature is undertermined. Since it loses carbon monoxide on heating, it contains a carbonyl bridge (2); the analysis shows that it contains a molecule of chemically combined alcohol which cannot be removed by acetic anhydride. It is probably the methoxyindone corresponding to XI.

The mechanism of formation of the indone X has already been considered (3). That of the chlorindone probably starts in the same way, with formation of the cyclopentadienone, which at once adds a second molecule of the chloride to form XI. The evidence is insufficient for further theorizing.

To learn more about substances such as the indone X, of which very few examples are known, it was treated with chromic acid, and an isomer was obtained. This isomer, when heated above its melting point, lost carbon monoxide. Hence, it contained a carbonyl bridge (2); this excluded any of the possible open chain formulas. It reverted to the starting material when treated with mineral acids, or spontaneously on long standing. This behavior led to the conclusion that the starting material was a mixture of two substances, one of which was oxidized by the chromic acid so much more rapidly than the other that the second could be isolated. The idea that it was a mixture was encouraged by the observation that the melting points of different preparations varied over a small range, though no other way of separation was found. An inspection of X reveals that geometrical isomerism of the decalone type is possible.

$$
\begin{array}{cc}
\text{X}a & \text{X}b
\end{array}
$$
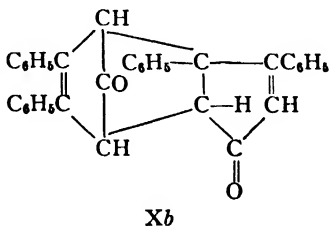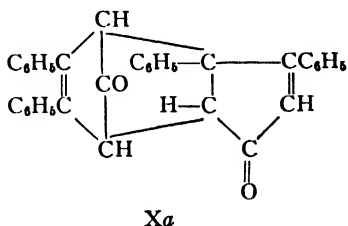
In the hydrindene series, to which these substances may be considered to belong, Hückel and others have shown that it is impossible to state with any degree of certainty whether the cis or trans form would be expected to be

more stable. Further, in the decalone series the cis is easily changed into the trans, presumably through enolization. In the case at hand, if it be assumed that the two forms are in a fairly mobile equilibrium, the changes described above are readily accounted for.

The problem of deciding which is cis is even less satisfactorily answered. Based on the observation that one form loses carbon monoxide on heating to give an unstable substance which then adds maleic anhydride (3), and upon an examination of space models of the second substance, of which only the cis form could add maleic anhydride without distortion, the cis arrangement Xa is tentatively suggested for that isomer. The trans linking Xb is thus left for the more stable form obtained after the chromic acid treatment.

The difference between the two is also shown by an examination of the results of pyrolysis. The new (trans) isomer gives an entirely different kind of substance, to which has been assigned Structure XII, although the evidence is not as complete as could be desired. The evidence is as follows:—

XII   XIII
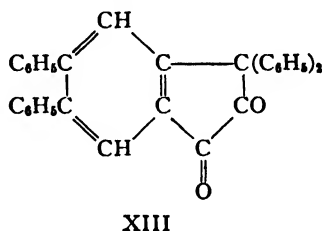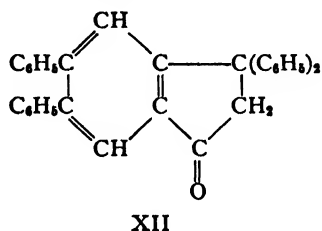
selenium dioxide gives a red diketone XIII, which is reduced back to the original substance by zinc and acetic acid. There are two hydrogen atoms which can be replaced by bromine or chlorine; the halogen is removed by reduction to give the starting material. It shows one addition in the Grignard machine, but does not give an oxime. It could be formed by the enolization of X, with the hydrogen atom returning to a carbon atom different from the one to which it was originally attached, with a concomitant 1,2 shift of a phenyl group. The necessary conditions of electromeric shift of the double bond possibly relate this to the corresponding rearrangement of tolane to
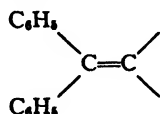
The diketone could not be degraded to a known substance. It showed addition of two molecules of methylmagnesium iodide in the Grignard machine. It formed a monoxime. It reacted with o-phenylenediamine, but from the analytical figures the product is an anil, rather than a quinoxaline; the presence of the two phenyl groups doubtless hinders the activity of the adjacent carbonyl so that it is relatively inactive. Sodium peroxide reacted but slowly and the product seemed unrelated to the starting material. None of the substances added maleic anhydride.

The behavior of the mixture on pyrolysis may be explained in this way—the cis (lower melting) form loses carbon monoxide at the melting point; this removes it from the equilibrium mixture. The trans isomer rearranges below the temperature at which it loses carbon monoxide, so that the mixture acts as a single substance and gives but one product.

Attempts* made to prepare some simpler 9–phenyldecalins have been unsuccessful. When Ruzicka's procedure (13) for the 9–alkyldecalins, which started with 1–methylcyclohexene, was adapted by substituting 1–phenyl-cyclohexene, it was impossible to get beyond the formation of the unsaturated ketone XIV; not even cyanoacetamide could be added to the latter.

XIV
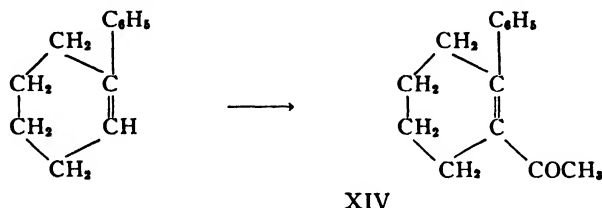
2,3–Dimethylbutadiene added to 2,5–diphenylquinone by Fieser's reaction (9, 10), but the untractable products did not have any of the expected properties.

Experimental

I. Work on Chloride IV; 3,4–Diphenyl–2–chlorocyclopenten–2–one–1

A mixture of 5 gm. of Vorländer's ketol (15) and 15 cc. of phosphoryl chloride was refluxed for 15 min., during which time the solid dissolved. The dark, cooled reaction mixture was added to 100 gm. of cracked ice, and the oil that separated was left to crystallize. It was dissolved in a minimum amount of hot alcohol and decolorized with Nuchar. After two treatments it formed pale yellow flakes, m.p. 142° C.†; the yield was 1.5 gm. (29%). It was very soluble in the usual solvents. Calcd. for $C_{17}H_{13}OCl$: Cl, 13.2%. Found: Cl, 13.2%.

A better quality of product was secured by the use of sulphuryl chloride, but most of the ketol was unattacked.

(1) The dinitrophenylhydrazone, prepared by Brady's procedure (5), separated in carmine needles from a 1:1 chloroform-methanol mixture; m.p. 216–217° C. Calcd. for $C_{23}H_{17}O_4N_4Cl$. : N, 12.5%. Found: N, 12.5%.

(2) Reduction: 3,4–diphenylcyclopentanone. One gram of the chloride was refluxed with 2 cc. of 48% hydriodic acid and 0.6 gm. of red phosphorus in 5 cc. of acetic acid for four hours, filtered hot, and the solution was poured into 70 cc. of water containing a little sodium bisulphite. The oil that separated was extracted with ether, and after appropriate manipulations, including a treatment with Nuchar, was poured into an equal volume of acetone. The

*Work of Dr. L. F. Halley.
†Melting points are corrected.

solid (or oil) was separated and crystallized with difficulty (because of its great solubility in everything except water in which it dissolves to some extent) from a 2:1 water-alcohol mixture. It separated in white needles, m.p. 92° C., and did not decolorize bromine. The same substance was secured in a less pure condition by a similar reduction of Vorländer's ketol. The dinitrophenylhydrazone, prepared as outlined above, formed dark red, iridescent needles, m.p. 228° C. Calcd. for $C_{23}H_{20}O_4N_4$: N, 13.5%. Found: N, 13.4%.

(a) Dehydrogenation of 3,4–diphenylcyclopentanone to 3,4–diphenylcyclopenten–3–one. On refluxing 0.2 gm. of the saturated ketone with 0.15 gm. of selenium dioxide in 10 cc. of dioxane for two hours, and working up, an oil was obtained which was immediately transformed into the dinitrophenylhydrazone. The latter, m.p. 233° C., was identical with the derivative prepared directly from the unsaturated ketone; the mixed melting point was not depressed. This reaction was repeated, always with the same result.

(b) 3,4–Diphenylcyclopenten–3–one and Vorländer's ketol gave 2,4–dinitrophenylhydrazones by Brady's procedure. The first formed red prisms, m.p. 233° C., while the latter separated in purplish-red needles, sintering above 230° C. and melting at 239° to 240° C. Calcd. for *(a)* $C_{23}H_{18}O_4N_4$: N, 13.5; *(b)* $C_{23}H_{18}O_5N_4$: N, 13.0%. Found: *(a)* 13.5; *(b)* 13.2%.

(3) Ozonolysis of the chloride. The chloride (0.1 gm.) in 50 cc. of pure ethyl acetate was treated with ozonized oxygen (12% ozone) for 70 min. The solvent was removed *in vacuo;* this left a gummy residue which deflagrated on heating. The ozonide was decomposed by water containing a little hydrogen peroxide and a few crystals of ferrous sulphate, the oil extracted with ether, dried, and added to an equal volume of acetone. On spontaneous evaporation, desylacetic acid was deposited, and was identified by its melting point (161° to 162° C.) and by the mixed melting point obtained with an authentic specimen.

Potassium permanganate destroyed the chloride, giving benzoic acid and a tar, but dilute chromic acid was almost without action.

(4) Action of basic reagents on the chloride. The latter was unaffected by silver nitrate, potassium acetate, and pyridine, but the chlorine was removed by piperidine, sodium carbonate, and sodium hydroxide. A suspension of 1.6 gm. of the chloride, 50 cc. of methanol, and 5 gm. of sodium carbonate was refluxed on the steam bath for a half-hour, and filtered. On standing, 1.1 gm. (70%) of white prisms, m.p. 208° C. after recrystallization from methanol-acetone, was obtained. It evolved carbon monoxide rapidly at 250° C. Calcd. for $C_{35}H_{28}O_3$: C, 84.7; H, 5.7; OCH$_3$, 6.2%; mol. wt., 496. Found: C, 84.7, 84.3; H, 5.7, 5.5; OCH$_3$, 6.0, 6.0%; mol. wt., 501.

This substance was unaffected by acetyl chloride, acetic anhydride, or hydrogen chloride in acetic acid. It did not give an oxime, but showed 1.2 active hydrogen in the Grignard machine.

II. Work with Chlorides I and II

(1) Rearrangement of I into II (Japp's) by hydrogen bromide. The procedure was the same as that previously described (3), in which hydrogen chloride in acetic acid was used. After four days, chloride II (m.p. 128° C.) and indone X were separated and identified by mixed melting points.

(2) The dinitrophenylhydrazones of I and II were prepared as outlined above; both separated in red needles from methanol-chloroform, with the same melting point, 216° C. Mixed melting points of all the dinitrophenylhydrazones were depressed 20° C. The derivative of I was unaffected by refluxing with alcoholic potassium acetate; the others were not submitted to this treatment. Calcd. for $C_{23}H_{17}O_4N_4Cl$: N, 12.5%. Found: N, (I) 12.6; (II) 12.5%.

(3) When 0.5 gm. of chloride I in acetone was treated with 0.4 gm. of powdered potassium permanganate and 0.3 gm. of magnesium sulphate for 24 hr., and worked up, 0.3 gm. of the indone X was isolated from the acetone extract.

(4) When the same chloride was warmed with 5% alcoholic silver nitrate, an abundant precipitate of silver chloride had formed after two minutes; the indone was isolated from the solution. Piperidine likewise gave the same substance.

When chloride II was refluxed for 1.5 hr. with 5% silver nitrate there was no action, the starting material being recovered unchanged. Piperidine hydrochloride was isolated after a treatment with this base, but no other crystalline material was found.* It was unaffected by ozone in ethyl acetate after 1.5 hr.

III. Work on Chloride III

(a) The 2,4–dinitrophenylhydrazone was prepared in the same manner as the others; it separated in red needles, m.p. 265° C. with decomposition. It did not contain chlorine. Calcd. for $C_{23}H_{16}O_4N_4$: N, 13.6%; mol. wt., 412. Found: N, 13.7, 13.8%; mol. wt., 435. It was unattacked after treatment with sodium pyruvate, picryl chloride or by sodium carbonate and methanol, by heating in a sealed tube with acetone or acetaldehyde, but was destroyed by alcoholic potash.

(b) A precipitate of silver chloride was formed immediately on the addition of alcoholic silver nitrate to a similar solution of the chloride; no crystalline material could be isolated from the filtrate.

(c) The chlorindone XI separated on refluxing for four hours a mixture of 1 gm. of the chloride, 5 cc. of methanol, and 30 cc. of 5% aqueous sodium hydroxide; it crystallized in thin prisms from methanol-acetone; m.p. 204° C. with evolution of carbon monoxide.

When 5 mg. was refluxed in 1 cc. of dilute sodium methylate for several hours and allowed to stand, 3 mg. of the indone X slowly crystallized.

*The indone gives a viscous product when boiled for any length of time with alcoholic potash; this explains why the English authors (7) did not repeat our work (3). We have had no difficulty, but avoided long heating.

IV. Preparation and Reactions of the Indone X*b*

1. *Action of Chromic Acid on the Indone X*

Five grams of the indone X, as obtained by the dehydration of anhydrace-tonebenzil, was dissolved in 25 cc. of boiling acetic acid, and a solution of 4 gm. of chromic trioxide in 20 to 30 cc. of hot acetic acid was slowly added through the condenser. When all the reagent had been added, the mixture was boiled for 15 min., and allowed to stand overnight, when 2.5 gm. of white needles was deposited; these were filtered and recrystallized from a minimum quantity of amyl ether or from a 1:1 chloroform-methanol mixture. The melting point was 264° C. with evolution of gas. The substance showed one active hydrogen and one addition in the Grignard machine. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2%; mol. wt., 464. Found: C, 87.3, 87.3; H, 5.4, 5.5%; mol. wt., 434.

The new substance was unaffected by maleic anhydride, and by four hours' refluxing with aqueous or alcoholic solutions of sodium hydroxide up to 30% strength. It did not form an acetal.

When it was refluxed with 25 cc. of acetyl chloride for one-half hour, and the red-brown solution allowed to cool, 4.5 gm. of white stubby prisms was deposited, m.p. 206° C., with evolution of gas. A mixed melting point with X showed no depression. Passage of dry hydrogen chloride through an acetic acid solution of X gave the same result.

(2) *Pyrolysis of Xb; Formation of 3,3,5,6–Tetraphenylhydrindone, XII*

Five grams of the substance was melted (265° to 270° C.) in a metal bath. After the evolution of gas had ceased, the light brown liquid was allowed to cool; it solidified to a glass. This was crystallized from 1:1 chloroform-methanol, as white needles, m.p. 182° C. The average yield was 85%. The product was soluble in chloroform, acetone, benzene, warm acetic acid; sparingly soluble in ethanol, and almost insoluble in methanol; it did not dissolve in dilute acid or alkali. In the Grignard machine it showed one addition. It did not add maleic anhydride. Calcd. for $C_{33}H_{24}O$: C, 90.8; H, 5.5%; mol. wt., 436. Found: C, 90.9; H, 5.6%; mol. wt., 453.

(a) *Reactions of XII*

(i) *Bromination.* One gram of the substance was dissolved in 15 cc. of acetic acid and a few bubbles of hydrogen bromide were passed through the solution; 1 cc. of bromine was then added and the mixture refluxed for 15 to 20 min., during which time hydrogen bromide was evolved. The white needles that were deposited were recrystallized from a methanol-chloroform mixture. The yield was 0.65 gm., m.p., 265° C. Calcd. for $C_{33}H_{22}OBr_2$: Br, 26.9%. Found: Br, 27.0%.

(ii) *Chlorination.* One gram of the compound was dissolved in 6 cc. of cold sulphuryl chloride. After standing for 15 min. the solution was cautiously poured into water and the mixture extracted with chloroform; the chloroform extract was dried over calcium chloride, and on slow evaporation deposited

a white solid which separated from acetic acid in white needles, m.p. 252° C. Calcd. for $C_{33}H_{22}OCl_2$: Cl, 14.1%; mol. wt., 505. Found: Cl, 14.3%; mol. wt.; 504.

Neither halide could be hydrolyzed by boiling with aqueous or alcoholic potassium hydroxide, or with silver acetate.

When 1 gm. of the chloride was refluxed with 1 gm. of mossy zinc in 60 cc. of acetic acid for four hours, the parent compound XII was regenerated in almost quantitative yield. There was no reaction in benzene.

(iii) *Miscellaneous.* It did not form an oxime. It gave tars on fusion with sodium hydroxide or sulphur.

(iv) *Oxidation; Formation of 3,3,5,6–Tetraphenylindandione–1,2, XIII.* A mixture of 2.7 gm. of the ketone, 0.7 gm. of selenium dioxide, and 20 cc. of dioxane was refluxed for six hours with stirring. After filtration from selenium and precipitation by dilution, the red solid was recrystallized from acetic acid; it separated (2.2 gm.) in reddish-orange rods, m.p. 199° to 200° C. It dissolved readily in benzene, acetic acid, and chloroform, but only slightly in the alcohols. It gave two additions in the Grignard machine, but did not add maleic anhydride. Calcd. for $C_{33}H_{22}O_2$: C, 88.0; H, 4.9%. Found: C, 87.9; H, 5.2%.

The oxime, prepared in the usual manner, formed light yellow needles that melted indefinitely at 200° C.; on standing, the needles changed to a powder. A trace of yellow prisms, m.p. 245° C., was also isolated. Calcd. for $C_{33}H_{23}O_2N$ (monoxime; 200° C.): N, 3.0%. Found: N, 2.8, 2.8%.

The solution from 2 gm. of *o*-phenylenediamine hydrochloride and 3 gm. of potassium acetate in 20 cc. of acetic acid was filtered, 1 gm. of the red diketone was added and after 14 min. refluxing the derivative had precipitated. It separated (1.2 gm.) in pale buff prisms, m.p. 272° C., from acetic acid; it is sparingly soluble in methanol, but dissolves readily in chloroform or acetic acid. Calcd. for $C_{39}H_{28}N_2O$: C, 86.7; H, 5.2; N, 5.2%. Found*: C, 86.9; H, 4.9; N, 4.9, 5.0%.

The action of other oxidizing agents, permanganate, chromic acid, or dilute nitric acid was too drastic and destroyed the substance. Sulphuric acid gave no useful product.

Reduction, by refluxing equal weights (1 gm.) of the diketone and zinc dust in 20 cc. of acetic acid for an hour, and the appropriate manipulations, regenerated the indone XII.

Action of sodium peroxide. When 1 gm. of the diketone in 10 cc. of acetone was shaken for four hours with an iced solution of 1.5 gm. of sodium peroxide in 10 cc. of water, 0.5 gm. of white needles was isolated from the acetone layer. Only a trace of solid was secured from the acidified aqueous layer. The needles melted at 257° to 258° C., but were insoluble in aqueous or alcoholic potash up to 50% strength. In the Grignard machine it showed

*The same values were obtained by the Dumas and Kjeldahl methods. The latter would not be expected to give the correct values with a quinoxaline (14).

two replaceable hydrogens but no additions. Found: C, 86.5, 86.5; H, 5.3, 5.6%; mol. wt., 431. With diazomethane it gave a new substance, m.p. 161 to 163° C. Found: C, 91.3; H, 5.9; OCH₃, 7.0, 7.3%.

V. From Work of Dr. L. F. Halley.   1–Phenyl–2–acetylcyclo-hexene–1

To a solution of 52 gm. of stannic chloride, 50 cc. of acetyl chloride, and 50 cc. of carbon disulphide, was added, over a period of two hours, 32 gm. of phenylcyclohexene in 50 cc. of carbon disulphide. The temperature of the solution was kept below −35° C. After four more hours the mixture was poured onto ice, the unsaturated ketone isolated by appropriate manipulations, and distilled. A yield of 21.5 gm. (54%) of a product, b.p. 145° to 147° C. at 7 mm., was secured. Calcd. for $C_{14}H_{16}O$: C, 84.0; H, 8.0%. Found: C, 84.2; H, 8.1%. The 2,4–dinitrophenylhydrazone separated from dilute alcohol in yellow needles, m.p. 165° C. Calcd. for $C_{20}H_{20}O_4N_4$: N, 14.7%. Found: N, 14.9%.

Reaction between 2,3–dimethylbutadiene and 2,5–diphenylquinone. A mixture of 20 gm. of the quinone, 50 cc. of the hydrocarbon, and 40 cc. of absolute methanol was heated in a sealed tube at 100° C. for five days; 3.6 gm. of a yellow solid was filtered, m.p. 264° to 266° C. From the solution, 16 gm. of a pale yellow glass-like substance, which could not be crystallized, was isolated. When 5 gm. of the latter in 100 cc. of boiling acetic acid was reduced by the gradual addition of 20 gm. of zinc dust, and the organic material precipitated by pouring into water, a solid, m.p. 169° to 170° C., after recrystallization from methanol or acetone, was obtained. Calcd. for $C_{24}H_{24}O_2$: C, 83.7; H, 7.0%; mol. wt., 344. Found: C, 83.5, 83.6; H, 7.0, 6.9%; mol. wt., 338. Found: (yellow solid) C, 86.9, 86.7; H, 4.4, 4.4%.

The reduced substance evolved hydrogen sulphide but no thiophenol when heated with sulphur, but was so badly charred as to be useless. Various oxidizing and reducing agents gave untractable, amorphous products, plus traces of benzoic acid. The high melting compound was recovered unchanged after two hours' fusion with caustic potash at 400° C.

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THE ACTION OF SATURATED STEAM ON DICALCIUM FERRITE AND ON TETRACALCIUM ALUMINOFERRITE[1]

By D. T. Mather[2] and T. Thorvaldson[3]

Abstract

The reactions which occur when dicalcium ferrite and tetracalcium aluminoferrite are exposed to saturated steam at temperatures between 100° and 300° C. were studied by determining the water absorbed and the optical properties and X-ray diffraction patterns of the products. The hydration of the probable products of decomposition under the same conditions was also studied. The main results were as follows:

Precipitated alumina, treated between 170° and 350° C. and then dried over calcium oxide or "dehydrite" at 21° C., gives a monohydrate of alumina. The product is the same whether the initial alumina contains excess combined water or has been dehydrated at any temperature below about 920° C. On similar treatment between 100° and 170° C. precipitated ferric oxide loses its water of hydration, giving a material with the crystalline structure of hematite. Tricalcium aluminate at temperatures between 150° and 300° C. forms the isometric hexahydrate.

On prolonged exposure between 100° and 300° C., dicalcium ferrite is completely decomposed to calcium hydroxide and ferric oxide (hematite). The first step appears to be a rapid direct hydration of the dicalcium ferrite to a dihydrate, followed by a rapid liberation of one mole of calcium hydroxide. Then follows a slow decomposition of the hydrated monocalcium ferrite with the formation of hematite.

Similar treatment of tetracalcium aluminoferrite at temperatures from 100° to 300° C. gives as final products the hexahydrate of tricalcium aluminate, calcium hydroxide, and ferric oxide (hematite). Here again a very rapid action appears to take place, producing the hexahydrate of tricalcium aluminate and hydrated monocalcium ferrite, the latter product then decomposing slowly to calcium hydroxide and ferric oxide as in the case of the dicalcium ferrite.

Introduction

The study of the hydration of substances present in Portland cement clinker has been mainly confined to the action of water on the silicates and the aluminates of calcium. Lately it has been shown that a compound of the composition $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (tetracalcium aluminoferrite) is present in Portland cement (2, 3) and probably present in aluminous cements. Another compound containing iron, dicalcium ferrite, is also probably present, possibly in solid solution with tetracalcium aluminoferrite, in aluminous cements (8) and in cements of the Portland type where the alumina is to a large extent replaced by ferric oxide, as in iron ore (Erz) cement. The experiments here reported were undertaken as a part of a general study of the reactions which occur when cement mortars are cured in saturated steam at high temperatures (4, 11, 12, 13, 14), and deal with the action of steam on dicalcium ferrite, tetracalcium aluminoferrite, and on some of the possible products of hydrolysis of these.

The available information on the hydration of dicalcium ferrite and tetra-calcium aluminoferrite refers to room temperature or in some cases to a constant temperature of 30° C. Lerch and Bogue (6) found that dicalcium ferrite hydrolyzes in all solutions of calcium hydroxide that are less than saturated, and is completely hydrolyzed when exposed to water under conditions which effect the removal of the lime liberated. Kühl and Wang (5) came to the conclusion that, when finely ground cement clinker containing dicalcium ferrite is shaken with saturated limewater at room temperature, no reaction occurs, while tetracalcium aluminoferrite under the same conditions forms hydrated tricalcium aluminate and hydrated monocalcium ferrite. Since the completion of the work reported in this paper (9), Bogue and Lerch (1) report that on hydration of dicalcium ferrite in the form of a water paste, stored for long periods at room temperature, an amorphous dicalcium ferrite hydrate is probably formed and that no free lime appears. The same authors report that tetracalcium aluminoferrite under similar conditions of hydration forms the hexahydrate of tricalcium aluminate and an amorphous phase, which they conclude is probably hydrated amorphous monocalcium ferrite.

Experimental Procedure

Small samples of the materials, usually in the anhydrous form, were weighed into covered platinum crucibles. These, carefully protected from dripping water, were heated in saturated steam in autoclaves. For the higher temperatures the steel autoclave was similar to that used by Morey (7). The heating element of chromel wire was wound on the insulated autoclave, the temperature was measured by means of standardized copper-constantan thermocouples and the temperature control was effected by a choke coil. After a period of treatment the crucibles were removed to a vacuum desiccator over calcium oxide or other drying agent until constant in weight. The steam treatment and drying were then repeated until no further change in weight was noted. Very great precautions were taken against any possible contamination of the material with carbon dioxide.

Experimental Results

For the interpretation of the experimental results obtained with dicalcium ferrite and with the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, it was necessary to study the behavior of the possible decomposition products in steam under corresponding conditions.

Calcium Oxide

Pure calcium oxide exposed to saturated steam at 150° C. hydrates quantitatively to the monohydrate (10). It was found that the same applies for all temperatures up to 300° C., the highest temperature used.

Alumina

Aluminum hydroxide was precipitated from a 2% solution of ammonia alum which was free from iron, the precipitate washed free from sulphate, redissolved in hydrochloric acid, and the precipitation and washing were

repeated. After this material was dried and ground to pass a 200 mesh sieve it contained 37% water (anhydrous basis). Exposure of this sample without further treatment to steam in the autoclave reduced the water held to one mole. The precipitated alumina after ignition to constant weight at temperatures up to 920° C. gave, on exposure to saturated steam in the autoclave at temperatures up to 350° C., a product of the same constant composition. For a large series of such experiments the maximum variation in the $H_2O : Al_2O_3$ ratio, after the product was dried to constant weight over calcium oxide, was from 1.01 to 1.06. This monohydrate of alumina did not lose any water when exposed for a month in vacuum over magnesium perchlorate trihydrate (aqueous tension $< 2 \times 10^{-3}$ mm.). The well defined X-ray powder pattern is identical for samples of the monohydrate produced in saturated steam at 150° C. and at 350° C. The readings of the pattern are given in Table I. This monohydrate of alumina thus appears to be a well defined compound. When the precipitated alumina was ignited to constant weight at 1100° C. it became very unreactive in steam.

TABLE I

READINGS OF X-RAY POWDER PATTERN FOR THE MONO-HYDRATE OF ALUMINA (FORMED IN STEAM)

Planar spacings	Estimated intensity
6.0	SS
3.14	SS
2.81	WW
2.34	SS
1.978	W
1.850	SS
1.765	W
1.655	M
1.523	M
1.445	S
1.382	M
1.307	S
1.210	W
1.175	W
1.156	W
1.131	W
1.110	WW
1.050	WW
1.018	WW

Ferric Oxide

This was prepared by triple precipitation of the hydroxide from a solution of ferric chloride. The final precipitate, dried at 105° C., had a composition represented by $Fe_2O_3 . 1.12H_2O$. On further drying over calcium oxide, the material lost about half a mole of water very quickly, but still retained somewhat more than half a mole after drying in vacuum over lime for 30 days. When the material having the composition $Fe_2O_3 . 1.12H_2O$ was exposed to saturated steam at 100° to 170° C., with subsequent drying over calcium oxide, water was lost until the molar ratio of $H_2O : Fe_2O_3$ was 0.20 or less. Similar results were obtained when the material after the steam treatment was dried at 21° C. over a saturated solution of potassium chloride (aqueous tension 16.1 mm.) as when dried over calcium oxide. A good X-ray powder pattern of the steam treated material was obtained and found to be identical with the pattern given by Hansen and Brownmiller (2) for hematite. The precipitated ferric hydroxide after ignition to constant weight at 1100° C. did not take up an appreciable amount of water when exposed to steam in the autoclave.

Tricalcium Aluminate

The hydrate formed when this substance is exposed to saturated steam at 150° C. has the composition $3CaO . Al_2O_3 . 6H_2O$ (11). The X-ray powder pattern for this hydrate is also known (12). It was found that temperatures

of steam treatment up to 300° C. gave the same compound as shown by the amount of water absorbed, the optical properties, and by the X-ray powder pattern.

Dicalcium Ferrite

This substance was prepared by heating an intimate mixture of calcium carbonate and ferric oxide in the proper proportion well below the dissociation temperature for dicalcium ferrite, 1436° C. The material, which contained no free lime after the heat treatment, was ground to pass a 200 mesh sieve.

The platinum crucibles containing the samples of dicalcium ferrite were ignited to constant weight at 1100° C. before exposure to steam in the autoclave at temperatures between 100° and 300° C. In some cases, instead of placing the dry ignited material in the autoclave, the samples were wetted with distilled water, in other cases with a saturated solution of calcium hydroxide. The final products in every case were the same, but the reaction was more rapid when the liquid phase was present. The higher temperatures also favored the reaction.

The maximum number of moles of water held per mole of $2CaO \cdot Fe_2O_3$ after steam treatment and drying over lime at room temperature was as follows: four samples treated at 100° C. for 46 days held from 2.00 to 2.02 moles of water. Six samples treated at 170° C. for 6 to 15 days held from 2.00 to 2.03 moles of water. Three samples treated at 300° C. for 5 to 9 days held from 1.96 to 1.99 moles of water.

The absorption of two moles of water per mole of dicalcium ferrite might be due to direct hydration to a dihydrate, or complete hydrolysis to calcium hydroxide and ferric oxide, or to partial hydrolysis, possibly with hydration of the products. Three methods were used to decide this question, namely: microscopic examination, determination of free lime in the product of hydration, and comparison of the X-ray diffraction patterns of the hydration product with those of calcium hydroxide and hematite.

The hydrated material examined under the microscope showed a number of plate-like crystals which were identified as calcium hydroxide. White's test for lime was positive and the procedure of Lerch and Bogue gave two moles of free lime per mole of the original dicalcium ferrite. Further, the hydration products gave good X-ray diffraction patterns, showing only the lines found in the patterns for calcium hydroxide and steam treated precipitated ferric hydroxide.

Four samples of dicalcium ferrite after exposure to steam at 100° C. for 46 days were placed for 141 days over a saturated solution of potassium chloride at 21° C. (vapor tension 16.1 mm.). The amount of water held varied from 2.61 to 3.01 moles per mole of the original substance. It has been shown that calcium hydroxide formed by direct hydration of lime (ignited calcium carbonate) in water vapor is capable of adsorbing large amounts of water (10), and it is probable that the same applies to both the

calcium hydroxide and the hematite formed under the conditions of these experiments. Subsequent drying of the samples for four days over calcium oxide brought the water content down to 2.00 or 2.02 moles.

The experimental work therefore indicates that the final products obtained on exposing dicalcium ferrite to saturated steam at temperatures between 100° and 300°C. are calcium hydroxide and anhydrous ferric oxide (hematite).

The above gives evidence only as to the final state of the system after long periods of steam treatment. There still remains the possibility that the dicalcium ferrite is first hydrated or partly hydrolyzed and hydrated, and that the complete hydrolysis represents a slow secondary reaction. A series of experiments was made in steam at 150° C.; the time of exposure to steam was varied, and both the free lime liberated and the amount of water held after drying over lime were determined. The dicalcium ferrite was in each case ignited to constant weight at 950° C. and moistened with saturated limewater before exposure to steam in the autoclave. The results are given in Table II, each value being the average of duplicates. (Allowance was made for the free lime added as limewater.)

TABLE II

TREATMENT OF DICALCIUM FERRITE IN SATURATED STEAM AT 150° C.

Time in autoclave, hr.	Molar ratio $H_2O : 2 CaO . Fe_2O_3$ after drying to constant weight over CaO	Molar ratio, $\dfrac{CaO \text{ (free)}}{2 CaO . Fe_2O_3 \text{ (original)}}$
4	1.73	0.97
6	1.91	1.07
12	1.94	1.29
24	1.94	1.38
62 (at 170° C.)	2.00	1.98

From Table II it is seen that nearly one mole of free lime (determined by the Lerch and Bogue procedure) is liberated on four hour treatment of the dicalcium ferrite in saturated steam at 150° C. The amount of water held by the product (after drying over calcium oxide) is much in excess of that accounted for by the free lime, so that one must assume that there was another stable hydrate present, probably $CaO . Fe_2O_3 . H_2O$. Microscopic examinations of the hydration products disclosed the presence of fairly large hexagonal plates of calcium hydroxide. The "four hour" sample showed a few of these present, together with dark masses which appeared to be amorphous. The X-ray diffraction pattern ($23\frac{1}{2}$ hr. exposure in the General Electric multiple powder apparatus) showed some *extremely* faint lines which appeared definitely to belong to the patterns for anhydrous dicalcium ferrite and calcium hydroxide. This indicated that almost all the dicalcium ferrite had been transformed at the end of the four hour treatment. The X-ray diffraction pattern for the "12 hour" sample gave a strong pattern for hematite and calcium hydroxide. The rapid liberation of the first molecule of lime and the long

time required for the liberation of the second molecule with the simultaneous formation of hematite indicates two distinct reactions. The fact that the "four hour" sample gives only a very weak X-ray diffraction pattern for hydrated lime is probably to be explained by the rapidity of the first reaction, the lime liberated not having yet formed to any great extent large enough crystals to give a pattern.

It seemed desirable to study the progress of the reaction during the first four hour period of steam treatment. A number of experiments were made with exposures in the autoclave of one, two, and four hours, the products being dried to constant weight over lime, and the water held and the free lime present being determined. The results obtained were somewhat erratic probably owing to the fact that the time required to raise the temperature of the autoclave to 150° C. and to cool it to room temperature was somewhat long and the conditions could not be controlled closely; suspended transformation also probably played a part. Thus sometimes the one hour treatment gave a greater effect than another two hour treatment. However, the results indicated rather conclusively that a large amount of hydration may take place before any lime is liberated. Thus in one case no free lime had been liberated at the end of one hour treatment at 150° C., although the material held 1.6 moles of water after drying to constant weight over calcium oxide at 21° C. In another case at the end of two hours 1.84 moles of water were held, while only 0.14 moles of free lime were present. At other times the amount of free lime was as high as 0.59 moles after a one hour treatment and as high as 0.80 after a two hour treatment, while the amount of water held varied from 1.5 to 1.85 moles per mole of original dicalcium ferrite.

It would thus appear that when dicalcium ferrite is exposed to saturated steam at 150° C. the following three reactions occur.

(1) $2CaO \cdot Fe_2O_3 + 2H_2O \longrightarrow 2CaO \cdot Fe_2O_3 \cdot 2H_2O$

(2) $2CaO \cdot Fe_2O_3 \cdot 2H_2O \longrightarrow Ca(OH)_2 + CaO \cdot Fe_2O_3 \cdot H_2O$

(3) $CaO \cdot Fe_2O_3 \cdot H_2O \longrightarrow Ca(OH)_2 + Fe_2O_3$ (hematite)

These reactions may overlap to some extent, but the third reaction is probably always slow as compared with the other two. The final products obtained are the same for all temperatures between 100° and 300° C.

Tetracalcium Aluminoferrite

This substance was prepared by heating an intimate mixture of pure calcium carbonate, precipitated alumina, and precipitated ferric oxide in the required proportions at somewhat below 1400° C. until a uniform product, in which free lime was absent, was obtained. The refractive indices and other optical properties checked with those given by Hansen, Brownmiller, and Bogue (3). The product was ground to pass a 200 mesh sieve.

The platinum crucibles containing the samples were ignited at 1100° C. to constant weight before exposure to steam in the autoclave. Moistening the sample before steam treatment accelerated the absorption of water by the material.

Samples were exposed to saturated steam at four temperatures, namely, 100°, 150°, 170°, and 300° C. The final amount of water taken up and held after drying over quicklime was the same at all temperatures, namely, 7.04 to 7.13 moles of water per mole of original $4CaO . Al_2O_3 . Fe_2O_3$. Microscopic examination of the product showed the presence of two crystalline substances, hexagonal plates with a refractive index $N_0 = 1.570$ and isotropic grains with N approx. 1.61. These therefore appear to be calcium hydroxide and the hexahydrate of tricalcium aluminate. The procedure of Lerch and Bogue gave 11.5% of free lime in the steam treated material, calculated on the basis of the anhydrous sample. This represents one mole of free lime per mole of original tetracalcium aluminoferrite. White's test for free lime made on the product dried over lime was, however, always negative. After heating the product at 500° C. for one hour this test became positive. It appears that a film of some kind protected the crystals of hydrated lime from the action of White's reagent.

From the microscopic examination, combined with the determination of the water held and the free lime in the hydration product, it appears that the reaction which takes place when the compound $4CaO . Al_2O_3 . Fe_2O_3$ is exposed to saturated steam at temperatures between 100° and 300° C. may be represented by:

$$4CaO . Al_2O_3 . Fe_2O_3 + 7H_2O \longrightarrow 3CaO . Al_2O_3 . 6H_2O$$
$$+ Ca(OH)_2 + Fe_2O_3 .$$
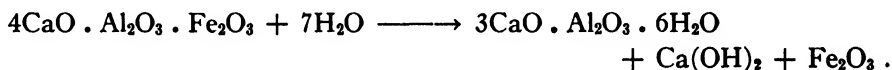
To confirm this, an intimate mixture of the substances on the right-hand side of the equation in the proportions indicated was prepared. (The Fe_2O_3 used was precipitated ferric hydroxide which had been exposed to saturated steam at 170° C. for seven days and then dried over lime.) The X-ray diffraction pattern obtained for this mixture was found to be identical with that obtained for the hydration product of $4CaO . Al_2O_3 . Fe_2O_3$ at 170° C. An X-ray pattern of the product obtained on exposing a sample of $4 CaO . Al_2O_3 . Fe_2O_3$ to steam at 170° C. for 30 days and then drying to constant weight over a saturated solution of potassium chloride at 21° C. (aqueous tension = 16.1 mm.) was also identical. The same applied to samples hydrated at 100° C. and then dried over potassium chloride. These products held more than nine moles of water, but on drying over quicklime the amount was reduced to seven moles.

These experiments give no evidence of the formation of hydrated monocalcium ferrite as a final product, although this substance is generally assumed to be one of the products of the hydration of $4CaO . Al_2O_3 . Fe_2O_3$ at room temperature.

The above refers only to the end products formed on treatment of tetracalcium aluminoferrite with saturated steam for long periods of time (five days or longer). A series of experiments was also made in which the sub-

stance was exposed to the action of steam for short periods of time. Table III represents the result of one such series. The samples were moistened with saturated limewater before exposure in the autoclave.

TABLE III

TREATMENT OF TETRACALCIUM ALUMINOFERRITE IN SATURATED STEAM AT 150° C.

Time in autoclave, hr.	Molar ratio H_2O : $4CaO$. Al_2O_3 . Fe_2O_3 after drying to constant weight over CaO	Molar ratio, $\dfrac{CaO \ (free)}{4CaO . Al_2O_3 . Fe_2O_3 \ (original)}$
1	7.13	0.15
2	6.74	0.23
4	7.06	0.43
6	7.01	0.41
12	—	0.62
24	7.26	0.70 ,
411*	7.08	0.99

* *This sample was exposed to steam in the autoclave without previous treatment with limewater.*

The data of Table III indicate that tetracalcium aluminoferrite absorbs seven moles of water very rapidly. The liberation of lime is a much slower process and is again comparable to the liberation of the second molecule of lime in the corresponding treatment of dicalcium ferrite. The probable interpretation is that tetracalcium aluminoferrite reacts rapidly with steam at 100° to 300° C. to form the hexahydrate of tricalcium aluminate and the monohydrate of monocalcium ferrite; the latter then decomposes slowly to give calcium hydroxide and hematite.

(1) $4CaO . Al_2O_3 . Fe_2O_3 + 7H_2O \longrightarrow 3CaO . Al_2O_3 . 6H_2O$
$$+ CaO . Fe_2O_3 . H_2O$$
(2) $CaO . Fe_2O_3 . H_2O \longrightarrow Ca(OH)_2 + Fe_2O_3 \text{ (hematite)}$
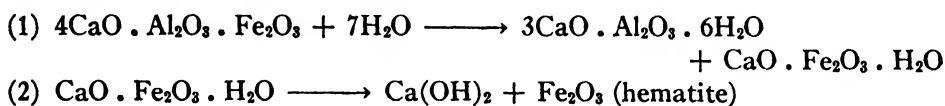
It is also possible that first a direct hydration of the tetracalcium alumino-ferrite takes place to give a hydrate with seven moles of water.

According to this interpretation the final reaction is the same for both dicalcium ferrite and tetracalcium aluminoferrite. Furthermore, the slowness of this reaction and the marked effect of temperature in increasing the rate of liberation of lime suggests that, on hydration of these substances at room temperature with a limited quantity of water, the monohydrate of monocalcium ferrite may be stable enough to represent an end product.

The deleterious effect on the strength of Portland cement mortars, produced by prolonged treatment in steam under pressure and the existence of an optimum time interval for steam curing which becomes shorter as the temperature is raised (14), is possibly at least partially explained by the slow second reaction.

Acknowledgments

The authors wish to express their appreciation to Dr. V. A. Vigfusson for help and advice in connection with the determination of optical properties and the comparison of X-ray patterns, to Mr. P. A. Puxley for making a series of experiments on the hydration of dicalcium ferrite and tetracalcium aluminoferrite, and to Dr. A. N. Winchell of the Department of Geology at the University of Wisconsin, in whose laboratory the X-ray photographs were made.

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HYSTERESIS OF WATER VAPOR ON CELLULOSE: INFLUENCE OF AIR[1]

By F. Walker[2], W. Boyd Campbell[3] and O. Maass[4]

Abstract

The amount of water sorbed from vapor by cellulose which had been previously dried was compared with that retained in equilibrium with the same atmosphere by the same sample after having been saturated. The difference between the two values was constant regardless of the presence of air within the limits 10^{-2} to 10^{-5} mm. air pressure.

The Effect of Degree of Vacuum on Hysteresis in Water Sorption by Cellulose

Introduction

Hysteresis loops extending from saturation to virtually zero relative vapor pressure have invariably been found by investigators who worked with small specimens of cellulosic material under carefully controlled conditions. In all cases moisture content values are higher during the desorption process than they are during the adsorption process for the same equilibrium relative vapor pressure.

In a recent paper Hamm and Patrick (3) have claimed that the phenomenon of hysteresis can be completely eliminated by carrying out the sorption measurements in the absence of permanent gases. These results are not explainable on the basis of the most generally accepted theory of water sorption by cellulose, so the present investigation was carried out with the object of attempting to produce a change in the magnitude of the hysteresis by changing the degree of vacuum under which the measurements were made.

Previous Work

In the case of certain artificial adsorbents such as silica gel, McGavack and Patrick (4) have attributed the hysteresis to the presence of adsorbed air, but Pidgeon (5) has recently shown that the absence of a hysteresis loop in Patrick's measurements was not due to a complete removal of air as he supposed, but to changing vapor pressure during sorption.

Patrick believes that cellulose differs from inorganic gels only in that permanent gases such as oxygen are removed from it with greater difficulty. He favors Zsigmondy's (13) explanation of hysteresis on the basis of a difference under adsorption and desorption conditions in the curvatures of the menisci of the liquids filling the capillary spaces, but this explanation is hardly applicable to elastic gels such as cellulose.

Urquhart and his co-workers (6–12) and Campbell (1) in experiments at reduced pressures (10⁻³ mm. of mercury) were unable to reduce the hysteresis effects for cellulosic materials.

Apparatus

The apparatus was designed with a view to facilitating evacuation to very low pressures, and essentially it consisted of a cell containing a helical quartz balance connected to a source of water vapor.

A diagram of the final arrangement of the apparatus is shown in Fig. 1. The cell, water bulb, and the tubing connecting them to the trap were made of Pyrex glass obtained fresh from the manufacturers, and the inside surfaces
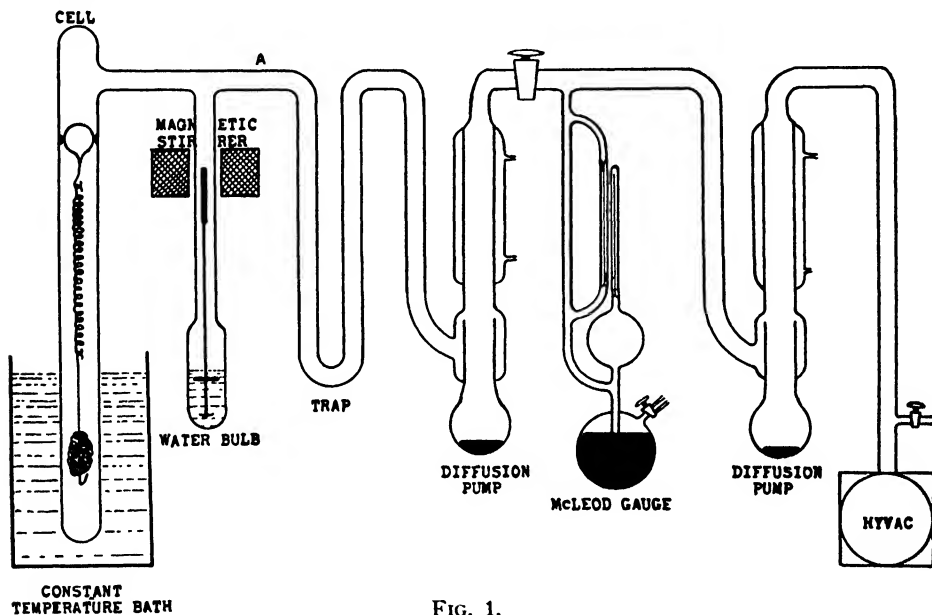
FIG. 1.

were washed once with distilled water because it was realized that glass treated with chromic acid cleaning solution presents a much larger surface for adsorption of gases.

Since speed of evacuation is limited largely by the diameter of the connecting tubing used, the cell was made of tubing of 41 mm. outside diameter and the trap and connecting parts of tubing of 22 mm. outside diameter.

A magnetic stirrer was placed in the water bulb, because continual breaking of the liquid surface hastens the attainment of vapor-pressure equilibrium. Owing to the fact that metals adsorb considerable quantities of gases, the stirrer was completely enclosed in glass.

The temperature of the cell containing the cellulose sample was thermostatically controlled at $28.00 \pm 0.05°$ C. The diffusion pumps used were the Cenco "Supervac" type. The McLeod gauge had a volume of 500 cc. and was calibrated to read 10^{-5}, 10^{-4}, 10^{-3}, and 10^{-2} mm. of mercury. It has been found (2) that in a system containing free mercury, small temperature

differences will cause a slow distillation of mercury, so in order to prevent condensation of mercury vapor on the sample, a trap was placed between the cell and the second diffusion pump; this trap was kept cooled by solid carbon dioxide or liquid air whenever the system was under vacuum.

The elimination of adsorbed gases from the glass tubing was an important function of the apparatus. To accomplish this, the tubing connecting the water bulb and cell to the trap was wrapped with resistance wire, as was also that section of the cell projecting above the liquid in the constant temperature bath. This enabled the apparatus to be baked out while the pumps were in operation. Only one stopcock was placed in the system, and this was done for convenience in making the low vacuum measurements.

Experimental Technique

After the apparatus had been assembled, all joints were tested for leaks with a high-frequency generator. When the apparatus was found to be free from leaks, the preliminary evacuation was carried out as follows: The water in the bulb was frozen, and the trap cooled with solid carbon dioxide; the system was evacuated until the McLeod gauge indicated 10^{-2} mm. The stopcock was closed, the ice allowed to melt and then refrozen. This procedure removed some of the dissolved air. The system was again evacuated to a pressure of 10^{-2} mm. and sealed off at A. The water bulb was surrounded with liquid air for 24 hr., and a reading of the extension of the balance due to the dry cellulose obtained.

Measurements of the hysteresis were carried out at this relatively high pressure. Since it was desired only to prove or disprove that the degree of vacuum has an effect on the hysteresis, it was decided to use one constant vapor pressure of water, namely that corresponding to a temperature of 0° C. This was a convenient point for two reasons. Any temperature control difficulties would be largely eliminated because the water bulb could be surrounded by a large Dewar flask containing enough chopped ice and water to last for the duration of a run. Also, the hysteresis at this relative vapor pressure amounts to a difference of about 12% in the amounts of water sorbed. This is equivalent to about 0.32% of the sample weight, and since the dry cellulose caused an extension of the balance of about 10 cm. which could be read to ± 0.001 cm., the weight of the sample was known with an accuracy of 0.01%. Under these conditions, any change in a hysteresis amounting to 0.32% of the sample weight would be readily measurable.

In order to ensure identical conditions for each run, the adsorption points were always determined with the material initially in a bone dry condition, and the desorption points with the material initially thoroughly saturated.

In making a run, the water bulb was left in solid carbon dioxide and acetone for 12 hr., and then a large Dewar flask containing ice and water was placed around the bulb. When the extension of the balance became constant within 0.01 mm. for a 10 hr. period, equilibrium was assumed to have been reached and a reading of the extension was taken. The water was removed from the bath controlling the temperature of the sample and the ice removed from

the water bulb; in this way, both sample and water were allowed to reach the same temperature. After the sample was saturated, a process that usually took about 12 hr., the temperature of the sample was again thermostatically controlled at 28.00 ± 0.05° C., and ice placed around the water bulb. When desorption was complete, a reading was taken as before. The difference between the two amounts of water held gave the magnitude of the hysteresis.

For the measurements under a high vacuum, the sealed-off part of the apparatus at A was reconnected and resistance wire wrapped around that part of the cell projecting from the constant temperature bath. The tubing of the water bulb and the tubing connecting it to the trap were similarly wrapped.

The water in the bulb was frozen and the Hyvac and one diffusion pump were started. The water was alternately frozen and melted four times under a pressure of 10^{-3} mm., so as to remove all traces of dissolved gas. Then the water bulb and trap were surrounded with liquid air, and all three pumps started. During the evacuation, current was passed through the heating coils so that the inner surfaces of the tubing were kept at about 350° C. A small section of the tubing at A, about 6 in. long, where the apparatus was to be sealed off, was kept at 550° C., so that when the actual sealing off took place, adsorbed gases would not be given off to any appreciable extent. The constant temperature bath was maintained at 55° C. in order to decrease to some extent the adsorbed gases on that part of the cell under the surface of the liquid; it is generally agreed that cellulose remains unchanged at this temperature.

After 36 hr. under these conditions, the McLeod gauge indicated 1×10^{-4} mm., so it was assumed that the apparatus would be at a pressure of 1×10^{-5} at most, because of the second diffusion pump. The apparatus was sealed off at A and a check reading made of the extension due to the dry cellulose. Measurements of the hysteresis were made as before.

Experimental Results

TABLE I

Condition	Time allowed, hr.	Time for equilibrium, hr.	Water on sample, %	Hysteresis
Air pressure, 10^{-2} mm. R.v.p., 16.15%. T=28.0°				
Saturated	18	14	15.75	
Desorption	19	7	2.91	
Dry	32	8	0·	
Adsorption	16	4	2.59	0.32
Saturated	23	14	15.74	
Desorption	20	7	2.90	0.31
Dry	17	8	0·	
Adsorption	12	4	2.59	0.31
Air pressure, 10^{-5} mm. R.v.p., 16.15%. T = 28.0°				
Saturated	26	14	15.75	
Desorption	16	7	2.66	
Dry	28	8	0·	
Adsorption	12	4	2.34	0.32
Saturated	24	14	15.75	
Desorption	13	7	2.66	0.32

Discussion

From the foregoing experimental results the conclusion may be drawn that there is no change in the hysteresis over a pressure range of 10^{-2} to 10^{-5} mm.; that is, within the experimental error, there is no effect from a thousandfold decrease in pressure.

Although Patrick (3) does not quote numerical values in his paper, he gives a graph showing the adsorption and desorption curves to be almost identical in the absence of permanent gases. However, his adsorption and desorption points at $2\frac{1}{2}\%$ moisture content differ by about 1 mm., which corresponds to 0.29% water on the scale used; this is certainly of the same order as the hysteresis in that region. Several other pairs of adsorption and desorption points at identical relative vapor pressures differ by a similar amount, and in general, Patrick's conclusion that hysteresis is eliminated seems scarcely justified by the experimental data.

In view of the present results, it seems very doubtful whether still lower pressures such as 10^{-6} or 10^{-7} mm. cause any change in the hysteresis. Any effect due to adsorbed permanent gases, at least in the amounts present in equilibrium with a pressure of 10^{-5} mm., which caused a sudden disappearance of the phenomenon of hysteresis would be difficult to explain on a theoretical basis.

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DENSITY-PRESSURE-TEMPERATURE RELATIONS OF THE HYDROGEN CHLORIDE-PROPYLENE SYSTEM IN THE CRITICAL TEMPERATURE-PRESSURE REGION.
REACTION VELOCITY NEAR THE CRITICAL TEMPERATURE[1]

By C. H. Holder[2] and O. Maass[3]

Abstract

The relation between the density, pressure, and temperature of a 2 : 1 and of a 1 : 1 mixture of hydrogen chloride and propylene has been determined over the temperature range 78° to 115° C. and up to pressures of 115 atm. These determinations are of interest in connection with the investigation of the influence of a "structure" of the liquid state on reaction velocity. Some preliminary measurements of reaction velocity in the critical temperature-pressure region have been made.

In the course of investigations (8–11) on the effect of molecular attraction on chemical reactions in the liquid state, it was observed by Maass and Sivertz (11) that a mixture of hydrogen chloride and propylene kept at room temperature and atmospheric pressure for 400 days showed no reaction. The corresponding mixture in the liquid state showed a reaction of 75% in 10 hr. at 0° C. Later, a parallel case was studied by Coffin and Maass (2, 3, 5). α- and β-Butylene reacted with hydrogen chloride in the liquid state, but in the gaseous state at 100° C. and 100 cm. pressure no reaction occurred in 40 hr.

At first sight it might be expected that the rather large difference in density between the liquid and gaseous states would be sufficient to cause or inhibit chemical reaction. With this in mind an investigation was undertaken by Sutherland and Maass (19), using the system hydrogen chloride-propylene, over a temperature range that extended well above the critical, and under pressure conditions such that the density of the gaseous mixture could be made to correspond to that prevailing in the liquid at lower temperatures. The results showed that the rate of reaction increases in a normal way in the liquid state, and that above the critical temperature the velocity of the reaction diminishes to such an extent as to introduce a discontinuity.

Largely as a result of these observations a study of the properties of substances in the critical pressure-critical temperature region was undertaken in this laboratory (6, 13, 14, 20, 22, 23). The observations made supported the hypothesis that the change from the liquid to the gaseous state involves something more than a mere change in concentration, and that in the liquid state of aggregation there exists a regularity in molecular distribution that gives to it what might be termed a "dynamic structure". Without specifying whether this "structure" takes the form of regional orientation (4, 10, 18), it is

true nevertheless that the results of Sutherland and Maass can be explained on the basis of such a hypothesis. If the existence of a "structure" promotes the velocity of a chemical reaction, its disappearance above the critical temperature will bring about a decrease in the rate of reaction, if this means that the change to a perfectly chaotic distribution of molecules has taken place. Some recent work by A. L. Geddes (7) and the investigations of Stewart and his co-workers on X-ray diffraction (1, 15, 16, 17, 18) indicate that, while this is probably the case when the two-phase system liquid-vapor is heated to the critical temperature, under pressures greater than the critical pressure the "dynamic structure" persists above the critical temperature.

It was therefore considered advisable to reinvestigate the reaction between propylene and hydrogen chloride, and as a preliminary to determine the pressure-volume-temperature relation of this two component system both above and below the critical pressure, in the temperature region where rate measurements were planned.

Experimental

The Apparatus

The apparatus is essentially the same as that used and described by Sutherland and Maass (19) and later by Winkler and Maass (21), and for this reason will not be described in detail here. The apparatus is depicted diagramatically in Fig. 1 (reproduced from Winkler and Maass's paper (21)). Definite amounts of the reactants, kept in storage flasks (not shown), were measured in calibrated volumes V_1 and V_2 and then transferred to P. The pressure of the mixture at a certain volume and temperature was recorded. By proper
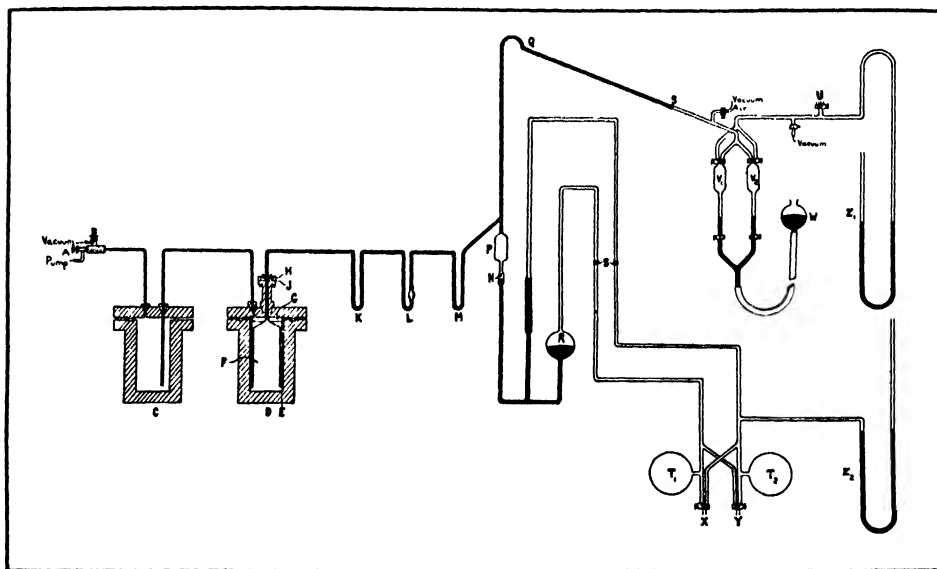
FIG. 1.

manipulation of the mercury supplies the gases were compressed into the small upper bulb of the reaction cell *L*. The gas could be kept there for any length of time by freezing the mercury in *K* and *M*. To stop the reaction the mercury seals were melted and the gases were returned to *P*, and from the pressure change observed the percentage reaction could be readily calculated.

Materials

Propylene was prepared as described by Maass and co-workers (3, 12) by the dehydration of isopropyl alcohol over alumina at 350° C. Purification was carried out by fractionating the liquid five to eight times by means of a carbon dioxide-acetone bath.

Hydrogen chloride was prepared by the action of c.p. sulphuric acid on recrystallized c.p. sodium chloride covered with c.p. hydrochloric acid. The gas was passed through four sulphuric acid scrubbers and condensed by means of liquid air. It was then fractionated, by the use of liquid air, four or five times.

Results

Densities were determined for both 2:1 and 1:1 mixtures of hydrogen chloride and propylene over a temperature range from 78° to 115° C. This was done by compressing a known weight of the reactants, measured out in the calibrated volumes V_1 and V_2, into the small reaction bulb whose volume was found to be 0.26 cc. by calibration with mercury. The Bourdon gauge was calibrated against the vapor pressure of hydrogen chloride at pressures of 950 and 1200 lb. per sq. in. A correction of 1% subtracted from the observed reading was found necessary. For a given mixture, whose density could be calculated from the following equation, the pressure required for a number of different temperatures was determined. This was then repeated for a mixture of different density.

$$\text{Density} = \frac{p_1 M_1 + p_2 M_2}{1000 \, RT} \times \frac{V}{v}$$

where p_1 and p_2 are pressures of propylene and hydrogen chloride respectively in V_1 and V_2,

  M_1 and M_2 are molecular weights of propylene and hydrogen chloride respectively,

  V is the volume of V_1 and V_2 = 93.3 cc.,

  v is the volume of the reaction bulb = 0.26 cc.,

  R is the gas constant,

  T is the temperature of gas in V_1 and V_2 in degrees absolute.

The results obtained are presented in Table I. Figs. 2 and 3 show pressure plotted against density for a given temperature. From these curves the density of a mixture can be determined from its temperature and pressure, even though it may not exactly fill the reaction cell. In this way the curves are of use experimentally.

TABLE I

Density	Temperature, °C.				
	78	85	95	105	115
	Pressure, atm.				

2 HCl : 1 C_3H_6

0.34	84.2	92.0	105.2	118.4	—
0.28	78.5	85.4	95.7	104.3	113.5
0.22	72.4	77.8	84.2	89.9	96.4
0.14	60.2	62.9	67.6	72.4	76.8
0.094	44.7	47.3	49.7	52.5	54.8
0.048	27.0	27.9	29.0	30.1	31.3

1 HCl : 1 C_3H_6

0.29	67.0	74.4	84.6	94.7	105.5
0.23	63.9	69.7	77.5	84.9	92.0
0.15	56.5	60.2	65.0	69.3	74.4
0.069	34.5	35.5	37.2	39.3	41.0
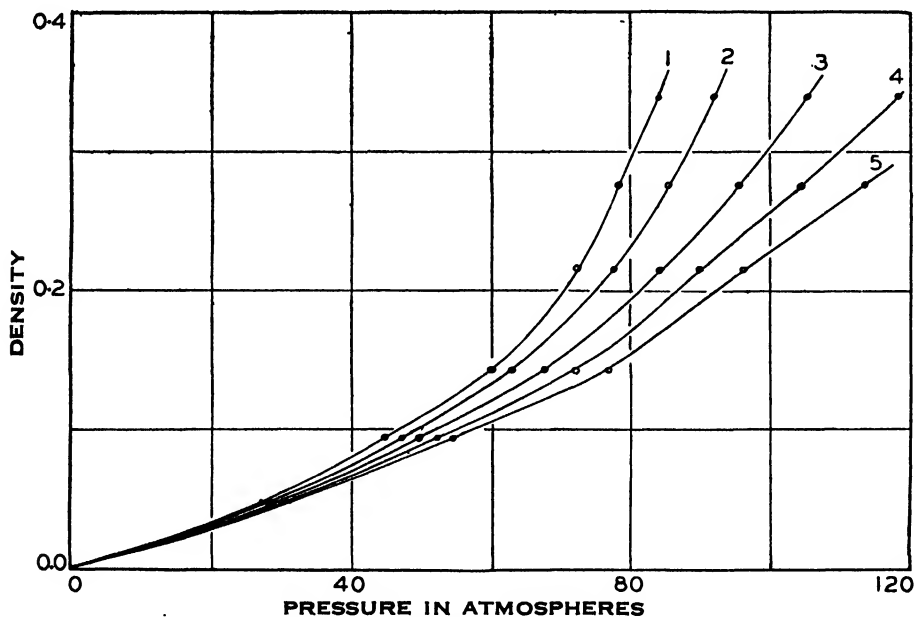
FIG. 2.   *Isotherms for 2 HCl : 1 C_3H_6 mixtures.   1. −78°.   2. −85°.   3. −95°. 4. −105°.   5. −115° C.*

FIG. 3. *Isotherms for 1 HCl : 1 C₂H₆ mixtures. 1. —78°. 2. —85°. 3. —95°. 4. —105°. 5. —115° C.*

Pressure readings could be made to within 1% of the pressure and 0.1° C. of the temperature. The greatest error involved is due to the position of the mercury at the ends of the reaction cell in the constricted parts of the tubing. Duplicate measurements could be made to within 0.01 of the absolute value of a density at the highest density and 0.002 at the lowest.

A test of the accuracy of the measurements is given by plotting the relation between pressure and temperature for isosteres, which should give a constant value for $\frac{dp}{dT}$. In Figs. 4 and 5 the straight line relation between pressure and temperature is made evident.

FIG. 4. *Isosteres for 2 HCl : 1 C₂H₆ mixture.*

FIG. 5. *Isosteres for 1 HCl : 1 C₃H₆ mixture.*

Discussion

Reaction Velocity Measurements

In the density measurements described, the absence of any reaction during the time that the measurements were made was confirmed by examining the pressure of the gas mixture at a constant volume before and after.

Some preliminary rate measurements have been made over a five hour period instead of the two hour period used by Sutherland and Maass. Essentially, their results have been confirmed. For instance, a 2 : 1 mixture at 105° C. and a pressure of 100 atm. in five hours showed only 2.5% reaction; when this mixture, after having been sealed in the reaction vessel at the same density was then cooled down to 50° C., a reaction of 3% in half an hour occurred. This is nine times as fast as the reaction above the critical temperature.

Sutherland and Maass found that the reaction above the critical temperature could be readily catalyzed by the presence of impurities such as traces of mercury chloride. This impurity had not been completely eliminated, and the apparatus is being renovated with this in view.

It is planned to make long time rate measurements over an extensive temperature-density range. For that purpose the data given in the first part of the paper are essential. Apart from this they are of interest

since so few accurate data are available for two component systems at high pressures, and this may be looked upon as the first of a number of two component systems to be studied in this laboratory.

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THE EFFECT OF ALCOHOLS ON THE TIME OF SET OF ALKALINE SILICA GELS[1]

By L. A. Munro[2] and C. A. Alves[3]

Abstract

Measurements have been made of the decrease in time of set of alkaline silica gels induced by a series of alcohols and acetone. Acetone, propyl, and butyl alcohols caused a marked increase in pH of the gel during setting. Glycol has a much smaller effect on setting time than the monohydric alcohols, while with glycerol the time of set of the alkaline gels was actually increased. Time of set is not strictly paralleled by the dielectric constant.

It has been shown by Hurd and Carver (2) that ethyl alcohol, acetaldehyde, and acetone increased the time of set of silica gels. Glycerol had only a negligible effect. This delayed setting was observed for gels having a pH range of from 5.2 to 6.0. Prasad and Hattiangadi (7) have also determined the effect of methyl, ethyl, and propyl alcohols, and acetone on the time of set of acid and alkaline gels. With alkaline gels these investigators observed an effect opposite to that obtained with acid gels viz., a decrease in the time of set. It is true that certain substances, the alkyl-amines, pyridine, and ammonia did decrease the time of set of acid gels, but it was noted that these increased the pH of the gel (2). Prasad (6) has shown that silica gels have a minimum time of set at about pH 7.6, the setting time increasing rapidly on each side of this optimum pH. Accordingly, any reagent that brings the pH of the acid gels nearer the isoelectric point would decrease the time of set. The alcohols, acetaldehyde, and acetone did not change the pH of Hurd and Carver's acid gels, so the alteration of the time of set was attributed to an effect of the addition agent alone.

During class experiments in the colloid laboratory it was noted, however, that the pH of alkaline gels was increased by the above substances. With these pure addition agents which had no effect on the pH of acid gels, an initial increase in pH was observed, and the final value on setting was appreciably different from that of the water gel. An increase in pH of an alkaline gel would be expected to increase the time of set (6). Prasad did not note any change in pH on addition of non-electrolytes to alkaline gels, but he did observe an induced decrease in the time of set. It was accordingly determined to study the effect of a longer homologous series of alcohols on the time of set of alkaline gels of known pH.

The time of set was determined by the tilted rod method described by Hurd and Letteron (3). Such a method measures merely the time required for gels to reach a certain degree of rigidity. Prasad and Parmar (8) have pointed out that gelation probably consists of three distinct processes: (1) formation of a sol; (2) coagulation, hydration, and agglomeration; (3) structural changes in rearrangements. Since acid and alkaline silica gels are very different in their optical properties during gelation, the method of Hurd would seem to be more suitable than the optical methods recommended by Prasad.

The time of set is quite sensitive to temperature changes (1, 4). The temperature of the laboratory was accordingly regulated to within one degree of the temperature of the thermostat (20° C.). A well stirred thermostat is necessary to dissipate the heat produced in mixing the acid and silicate. The required amounts of acid, water, and addition agent were placed in 50 cc. Pyrex beakers in the thermostat. A 25 cc. portion of the standard silicate solution was pipetted into beakers that had previously held 25 cc. of silicate and had drained for six seconds. This assured delivery of a constant volume of silicate. The silicate was added to the acid solution with rapid stirring, care being taken that the whole operation involved the same length of time (10 sec.). The stop watch was started as soon as all the silicate was added. In all experiments on the alkaline gels the acetic acid used was prepared by diluting 100 cc. of glacial acetic with 500 cc. of water. Standard sodium silicate solution of sp. gr. 1.1563 was obtained by dissolving Baker's c.p. "crystalline" sodium silicate. This solution contained 6.6% of silicon dioxide. It was diluted with distilled water to give a solution containing 3.3% of silica. Addition agents were of Eastman's best grade.

The attempted use of the antimony electrode for the pH determinations was abandoned, as it has been shown by Kolthoff and Hartong (5) that this gives incorrect readings unless the medium is stirred continuously. As all the writers' experiments were carried out in alkaline solution, the quinhydrone method used by Hurd and Carver (2) for acid gels could not be employed either. The pH of the writers' gels was estimated by means of indicators. The time of set and pH were determined in portions of the same mixture. No indicator was added to the portion upon which determination of the time of set was carried out; this avoided any influence of the indicator itself on the time of set.

The initial pH was 10.4 in all cases in which the amount of added substance was 0.5 cc. This increased to 10.5 with higher concentrations. The pH was found to change on setting—the pH of the water-acetic acid gel increasing to 10.6, while with acetone and n-propyl alcohol the final pH changed from 10.6 to 11.2 as the amount of added substance was increased to 2.0 cc. The effect of addition agents on the pH of the gel as determined colormetrically is illustrated by Table I and the results for the alcohols studied are given in Table II.

TABLE I

CHANGE IN FINAL pH WITH BUTYL ALCOHOL AND ACETONE AS ADDITION AGENTS

Cc. added	Tert. BuOH (22° C.)			Acetone (Table III)	
	Time of set, sec.	Initial pH	Final pH	Initial pH	Final pH
0.0	240	10.0	10.5	10.4	10.6
0.5	120	10.4	10.6	10.4	10.7
1.0	80	10.4	10.6	10.5	10.8
1.5	55	10.4	10.6	10.5	11.0
2.0	40	10.4	10.6	10.5	11.2

TABLE II

Concentration of added substance		Time of set, sec.	Concentration of added substance		Time of set, sec.
Cc. in 50 cc. gel	Moles per l.		Cc. in 50 cc. gel	Moles per l.	
Methyl alcohol			*n-Propyl alcohol*		
0.0	0.0	210	0.0	0.0	210
0.5	.248	134	0.5	.134	116
1.0	.50	103	1.0	.27	69
1.5	.74	86	1.5	.40	43
2.0	.99	64	2.0	.54	32
2.5	1.24	50	2.5	.67	21
3.0	1.49	44	3.0	.80	9
Ethyl alcohol			*Iso-propyl alcohol*		
0.0	0.0	210	0.0	0.0	214
0.5	.172	115	0.5	0.131	108
1.0	.34	74	1.0	.26	68
1.5	.52	49	1.5	.39	42
2.0	.69	31	2.0	.52	30
2.5	.86	22	2.5	.66	18
3.0	1.03	15	3.0	.79	10
n-Butyl			*Sec-butyl*		
0.0	0.0	210		0.0	214
0.5	.109	120		.109	123
1.0	.22	67		.22	65
1.5	.33	42		.33	39
2.0	.44	30		.44	21
2.5	.55	19		.55	14
3.0	.65	14		.65	ppt.
Iso-butyl			*Tert-butyl*		
0.0	0.0	212		0.0	215
0.5	.11	114		.106	110
1.0	.22	67		.21	64
1.5	.33	42		.32	39
2.0	.44	28		.42	21
2.5	.55	ppt.		.53	ppt.

Fig. 1 shows the data for Table II; the time of set for similar volumes of added substance is plotted for individual members. The curve obtained for 0.5 cc. of added substance is quite irregular. However, the curves for higher
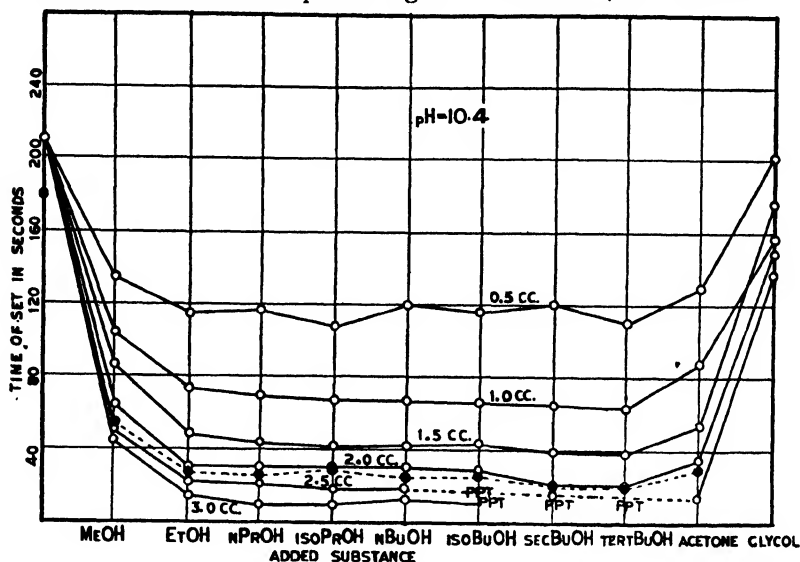
FIG. 1; ●, earlier experiment.

concentrations show regular gradation in effects; this indicates that the effect of changes in pH is less than the specific effect of the addition agent. The order of effects for similar volumes seems to be:— tert. BuOH = sec. BuOH > iso-, n-, BuOH, n- and iso-PrOH > EtOH > acetone > MeOH. The same order is shown within experimental error in a previous experiment on the addition of 2 cc. of addition agents to a gel having a setting time of 180 sec. at 18° C. This is shown graphically by solid points and broken line, Fig. 1.

For the higher concentrations of the butyl alcohols, an amorphous precipitate was formed instantaneously with sometimes subsequent coagulation of the supernatant sol. In Figs. 2 and 3 the times of set are plotted against molar concentrations, calculated from the specific gravity and molecular weight.

TABLE III

Added substance, cc.	Acetone		Glycol		Glycerol	
	Moles per litre	Time of set, sec.	Moles per litre	Time of set, sec.	Moles per litre	Time of set, sec.
0.0	—	210	—	215	—	216
0.5	0.137	129	0.179	202	0.137	244
1.0	.274	87	.358	166	.274	250
1.5	.411	54	.537	156	.411	253
2.0	.548	34	.716	149	.548	255
2.5	.685	14	.895	137	.685	260
3.0	.822	ppt.	1.074	136	.822	265
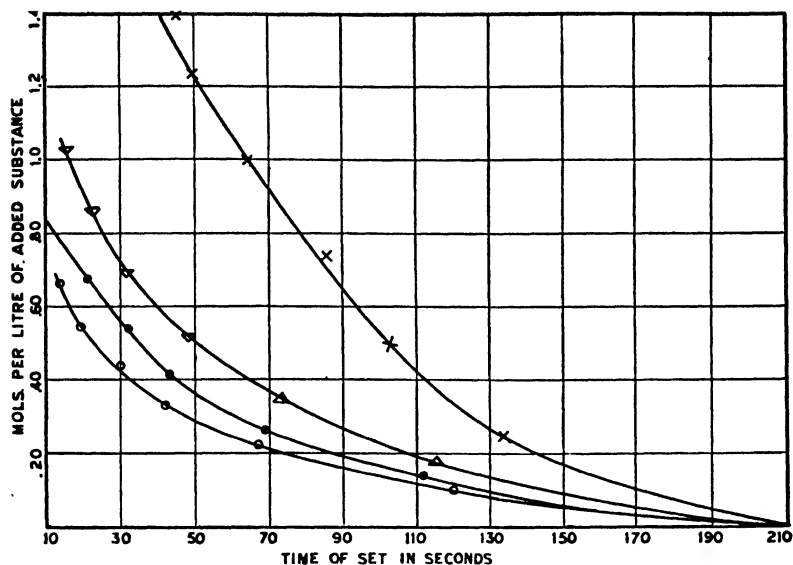
FIG. 2. ✕, *methyl alcohol;* △, *ethyl alcohol;* ●, *n-propyl alcohol;* ○, *tert. butyl alcohol;* *pH, 10.4.*
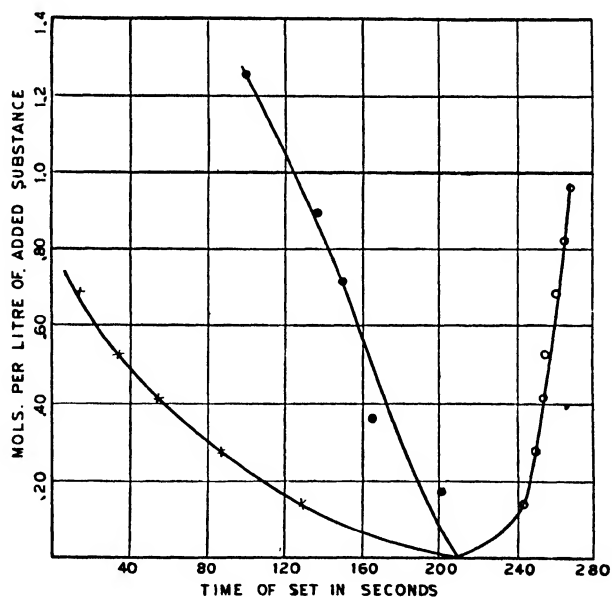
FIG. 3. *pH, 10.4;* ✕, *acetone;* ●, *ethylene glycol;* ○, *glycerol.*

The most striking results of this investigation are: (1) the small effect of glycol as compared with that of acetone and propyl alcohol, compounds of similar molecular weight; and (2) the actual reversal of the effect as shown by glycerol (Table III).

It has been noted by Hurd and Carver (2) that glycerol has a very slight effect on the time of set of acid gels. Their observation has been checked in

the case of a very slow setting gel of pH 5.1 from silicate containing 3.3% silicon dioxide (Table IV).

There is, therefore, a slight increase in the time of set in acid gels which is apparently not proportional to the concentration.

The change in time of set induced by the addition agents is approximately parralleled by the gradation of the dielectric constants in this series. A change in the dielectric constant of the dispersion medium would influence the electrical layer and hence the stability of the sol. It is known that a negative sol can be changed to a positive one by the addition of alcohol (7). The observed change in pH of the writers' alkaline gels with the addition of non-electrolytes may be due in part to the changed dielectric properties.

There are, however, several anomalies which, as Prasad points out (7), "cannot be explained by the diminution of the dielectric constant and hence change in density of the charge on the particle." The discrepancies quoted by him may be supplemented from the present investigation. Acetone and *n*-propyl alcohol have almost identical dielectric constants at 20° C., but have dissimilar effects on the time of set. Isobutyl and tertiary butyl alcohols should show a greater divergence in the time of set.

The behavior of glycerol cannot be accounted for by the retarding effect of greater molecular size. If such were true a similar increase in time of set would be observed with acid gels. Table IV shows that this is not the case.

TABLE IV

Expt.	Added substance, cc.	Time of set, hr.	sec.	Expt.	Time of set, hr.	sec.
1	0.0	13	30	7	13	35
2	1.0	13	53	8	13	50
3	2.0	13	55	9	13	50
4	3.0	14	0	10	14	03
5	4.0	14	0	11	14	0
6	5.0	13	55	12	13	58

Weber and Lederer (9) have recently determined the dehydrating power of addition agents. Gelatin gels were treated with a series of alcohols and the amount of dehydration was measured. Monohydric alcohols were found to withdraw water in the order, PrOH, EtOH, MeOH. This is the same order as their effect on the time of set. Glycols were observed to have a stronger dehydrating action than the monohydric alcohols, and the effect became greater with increase in molecular weight and number of hydroxyl groups in the higher alcohols. If the effect of addition agent on the time of set is due to dehydration of the micelles, one might expect on the basis of their experiments a very short setting time with glycol and glycerol.

It would seem that the anomalous behavior of glycerol would justify further study.

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THE PREPARATION OF PURE METHANE FROM NATURAL GAS[1]

By E. H. Boomer[2], C. A. Johnson[3], and V. Thomas[4]

Abstract

A method of removal of all hydrocarbons in natural gas other than methane is described. Pyrolysis of the higher hydrocarbons under such conditions of temperature and rate of flow that methane is not affected is used. The products of pyrolysis are easily removed by common chemical methods.

Introduction

It was necessary for the work proceeding in these laboratories, that a fairly large supply of gas be available consisting only of methane with a small proportion of nitrogen. Natural gas that is high in methane, containing about 3.5% higher hydrocarbons and 5.7% nitrogen was available from the Viking field. The usual method of separating the methane by liquefaction and distillation was not practicable under the circumstances, and another method, based on experience obtained in experiments on pyrolysis, was devised. Briefly, the method consisted of controlled pyrolysis of the natural gas, resulting in the decomposition of all hydrocarbons but methane, followed by removal of the decomposition products. The method has been applied to Viking natural gas only, but is applicable to any natural gas. The presence of sulphur compounds in the gas is not detrimental, and the sulphur is removed completely in the process. It is necessary only to determine, by means of a few experiments, the temperature and rate of flow that produces decomposition of all hydrocarbons other than methane. The method is presented as an alternative to the use of low temperature distillation in the separation of methane from natural gas. In the event that nitrogen is undesirable, separation by liquefaction must be employed.

Apparatus and Operation

The supply of natural gas was connected to the apparatus shown in Fig. 1 through the flowmeter A. The rate of flow of gas was regulated by the stop-cock shown. The drying tower, B, contained calcium chloride and served to remove water vapor from the gas. The gas then entered a quartz pyrolysis tube, $\frac{3}{4}$ in. in diameter, heated over a 12 in. length by means of an electric furnace. The tower, D, contained glass wool which acted as a filter and removed most of the suspended carbon and oily matter formed in the gas during pyrolysis. The next tower, E, contained soda-lime, and it removed hydrogen sulphide formed in the pyrolysis of organic sulphur compounds

in the natural gas.   Activated coconut charcoal, placed in the large bottle, F, removed the vapors of liquid hydrocarbons such as benzene and considerable quantities of the heavier, unsaturated gaseous hydrocarbons produced on pyrolysis.   From F the gas entered the bottom of the sulphuric acid scrubber,
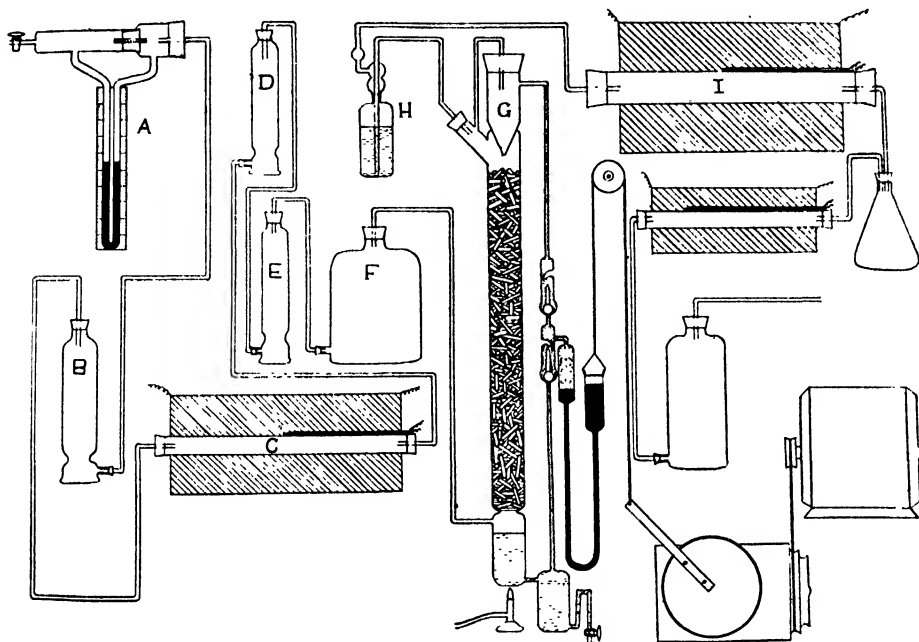
FIG. 1.   *Apparatus for pyrolysis and removal of higher hydrocarbons in natural gas.*

G.   The tower was packed with short pieces of glass tubing and was charged with 400 cc. of 95% sulphuric acid containing 1% of silver sulphate.   The acid was heated to about 70° C. by means of a gas burner and was circulated continuously through the scrubber by means of the glass and mercury pump shown.   Olefines and other unsaturated compounds in the gas, as well as sulphur compounds, were removed completely by the sulphuric acid and some sulphur dioxide was produced.   The scrubber, H, containing sodium hydroxide solution, removed any sulphur dioxide in the gas.   The gas passed next through two copper oxide tubes, I, heated electrically to 320° C.   Here, hydrogen and carbon monoxide were oxidized to water and carbon dioxide respectively.   Two copper oxide tubes were necessary with a water trap between them to ensure complete removal of hydrogen and carbon monoxide. The first tube contained about five pounds and the second tube about one pound of copper oxide.   The carbon dioxide was removed by soda-lime in the bottle shown.   The gas, now methane, was stored in water-sealed gas holders.

A series of experiments showed that at 780° C., all the ethane and heavier hydrocarbons were decomposed in the pyrolysis tube; this process yielded olefines, aromatics, carbon, carbon monoxide, and hydrogen.   In addition, the sulphur compounds in the gas were converted largely to hydrogen sulphide.

The rate of flow as measured on the flowmeter, *A*, could be as much as 1000 cc. per min. but could not be less than 800 cc. per min. without some decomposition of methane taking place. The Viking gas used here was of the same composition as that described above and contained some ten grains of sulphur per 100 cu. ft. This yielded a gas free from sulphur; its composition was: methane, 94.5; nitrogen, 5.5%. There were only slight variations from this composition corresponding to variations in the temperature of the pyrolysis tube.

The apparatus, while of many parts, was quite simple to operate. It required no attention other than that required for replacement of chemicals, and was operated 24 hr. per day. The average production of gas per day was 40 cu. ft. Once a day the sulphuric acid was replaced, and once every ten days the calcium chloride, soda-lime, and sodium hydroxide scrubbers were refilled. About once a month the copper oxide was re-oxidized by passing air through the tubes, and the coconut charcoal was activated by steam treatment.

The consumption of materials per 100 cu. ft. of gas prepared was as follows: 1000 cc. technical, 95%, sulphuric acid, 50 gm. calcium chloride, 80 gm. soda-lime, and 20 gm. sodium hydroxide. Approximately 1500 watts of electric power were required to heat the furnaces.

THE PRECISION COMBUSTION ANALYSIS OF GASES[1]

By E. H. Boomer[2] and C. A. Johnson[3]

Abstract

A precise method of determining the hydrogen and carbon content of gases is described. The method employs, in part, the methods of ultimate organic analysis by combustion over copper oxide and collection of the carbon dioxide and water formed. It is particularly suited to the analysis of combustible gases containing vapors of volatile liquids.

Introduction

In connection with other work proceeding in these laboratories it was necessary to analyze quantitatively gas mixtures, substantially methane, containing small amounts of hydrocarbon vapors. A procedure involving distillation or freezing out of the vapors was not practicable, and owing to the small amounts of vapors present the usual combustion analysis on the Orsat type of apparatus was quite inadequate.

A method of analyzing such mixtures to give precisely the carbon and hydrogen content was devised. This method is applicable to any gas for which such information is sought. The principles employed are those used in ultimate analysis by combustion for carbon and hydrogen as commonly practised with liquids and solids. Briefly, the method consists in oxidizing a measured sample of gas in a closed system to carbon dioxide and water, which are collected and weighed in the usual absorption vessels. Hot copper oxide, plus 1% of cerium oxide as promotor, served as the oxidizing agent. As is well known (1, Chap. 13) the rate of oxidation of methane by copper oxide is slow, and, while cerium oxide speeds up the reaction appreciably, provision has to be made for recirculation of the gases. Experiments showed that several minutes contact was necessary when the copper oxide was at 800° C. Finally, to ensure complete oxidation to carbon dioxide and water, oxygen was admitted to the circulating system. In order to handle gases containing sulphur or nitrogen compounds, the usual additions of a reduced copper spiral and granulated lead chromate to the combustion tube may be made. This report covers the procedure necessary in the absence of sulphur or nitrogen compounds.

The method was given a rigorous test by analyzing known mixtures of methane, nitrogen, and benzene vapors. The deviations between the calculated and observed weight percentage of benzene and methane was less than 0.5%, and on unknown gas mixtures duplicates were obtained showing similar agreement.

The errors were controlled principally by the weight of carbon dioxide and water; any errors in these data, which are correct to within 0.1 mg., being magnified in the process of calculation. While a high degree of precision is unnecessary in the application for which the method was devised, the precision of the analysis can be improved simply by using larger gas samples.

Apparatus

The apparatus is shown in diagramatic form in Fig. 1. The gas sample was measured in the calibrated pipette *C*. The pipette volume, at 25° C., was 183.93 cc. The temperature was determined by means of a calibrated
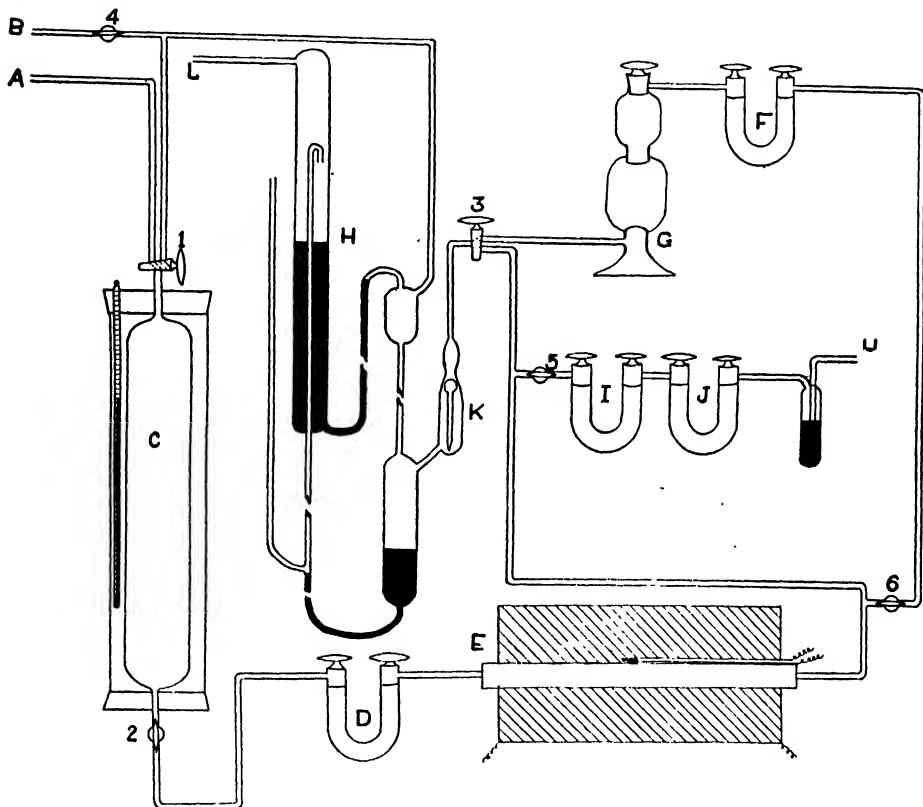
FIG. 1.   *Apparatus for precision combustion analysis of gases.*

thermometer immersed in a water jacket surrounding the pipette. The pressure was measured by means of a mercury manometer connected to a gas storage system (not shown), which was connected at *A*. The whole apparatus could be evacuated by mercury diffusion pumps connected at *B* through stopcock 4. A modified Sprengel pump, *H*, was employed to circulate the gas in the apparatus. This pump was operated automatically from a water jet pump attached to *L*. A check valve, *K*, acted as a trap against mercury spray and prevented entrance of mercury to the rest of the apparatus

in the event of failure of the evacuating system.   The copper oxide tube, E, 15 in. long and ¾ in. in diameter held about 200 gm. of copper oxide-cerium oxide mixture.   The quartz tube was protected from the action of hot copper oxide by a lining of thin asbestos paper.   The temperature of the copper oxide was maintained at $800° \pm 10°$ C. by means of an electric furnace as shown, the temperature being indicated by means of a milli-voltmeter and thermocouple.   This temperature was sufficiently high to oxidize rapidly and completely the hydrocarbons in the gas.

A magnesium perchlorate drying tube, D, which absorbed the water produced on combustion, was placed immediately after the combustion tube. Provision was made for warming the connection between the combustion tube and the absorption tube.   A soda-lime absorption bulb, G, and the guard tube, F, containing magnesium perchlorate, were connected on a by-pass line through stopcocks 3 and 6.   An oxygen supply was connected at U, carbon dioxide and water being removed by soda-lime in tube J and by magnesium perchlorate in tube I.

Operation

The drying tube, D, and carbon dioxide absorption assembly, G and F, were weighed, filled with oxygen at atmospheric pressure, and connected to the apparatus with clean, sulphur free, pressure tubing, the joints being wired.   The temperature of the combustion furnace was raised to 800° C. and the whole apparatus, except the absorption tubes, was evacuated through stopcock 4.   The absorption tubes were of the type having built-in stopcocks.   The mercury supply and discharge tubes connected to the Sprengel pump were shut off by screw clamps.   With stopcock 2 closed and stopcock 1 opened to the gas storage system through A, a sample of gas was passed into the pipette, C, the pressure and temperature being recorded.   With stopcocks, 3, 4, 5, and 6 closed, stopcock 1 reversed and stopcock 2 open, the gas sample.was allowed to expand into the apparatus.   The level of the mercury reservoir of the Sprengel pump was adjusted to match the gas pressure in the apparatus and circulation was then started.   The rate of circulation was about 100 cc. per min., and in 15 min. oxidation of the gas was nearly complete.   Circulation was stopped momentarily, stopcock 3 reversed, and 6 opened to put the carbon dioxide absorber in the circulating system.   Stopcock 5 was opened and oxygen allowed to flow into the system. After adjusting the level of the mercury reservoir of the Sprengel pump to match atmospheric pressure, circulation was started again.   Oxygen entered the system automatically as the remaining traces of combustible gases were oxidized and the copper was reoxidized.   After 45 to 60 min., the absorption systems were removed and weighed.

For gases containing only three components, the carbon-hydrogen analysis obtained above in conjunction with a density determination permitted the calculation of the composition.   An analysis took from 1.5 to 2.0 hr. but of this time less than half an hour was actually consumed in making adjust-

ments and weighings. Little experience is required to obtain excellent results. It is essential, of course, to have no leaks in the system and to take the usual precautions in determining the weight increases of the absorption tubes. The chief precaution necessary occurs when a combustion tube is newly installed. The tube and its contents must be heated to 800° C., or somewhat higher, while being evacuated until gas ceases to be evolved.

TABLE I

ANALYSIS BY COMBUSTION AND DENSITY MEASUREMENTS OF SYNTHETIC AND UNKNOWN
MIXTURES OF METHANE, NITROGEN, AND BENZENE VAPOR

Weight per cent from make-up:							
Benzene	15.31		8.88		—		—
Methane	74.55		79.83		—		—
Density, gm. per litre	0.8730		0.8152		0.8551		0.8384
Sample volume, cc. at N.T.P.	158.3	158.9	95.35	95.06	95.33	95.03	95.43	95.50
Combustion data:							
Carbon dioxide, gm.	0.3546	0.3542	0.1937	0.1931	0.2190	0.2195	0.2119	0.2115
Water, gm.	0.2479	0.2477	0.1454	0.1449	0.1551	0.1555	0.1530	0.1519
Weight per cent from analytical data:							
Benzene	15.32	15 25	8.92	8.90	15.04	15.10	13.04	13.09
Methane	74.60	74.22	79.80	79.80	79.29	79.75	80.40	80.12

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EQUILIBRIA IN TWO-PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

I. METHODS AND APPARATUS[1]

By E. H. Boomer[2], C. A. Johnson,[3] and G. H. Argue[4]

Abstract

An apparatus was devised by means of which a gas and a liquid could be brought into equilibrium at any desired pressure up to 370 atm. and temperatures from 25° C. to above 100° C. Provision was made for the taking of samples of known volume from the liquid and gas phases in equilibrium. Analytical methods were developed to yield phase densities and compositions.

Introduction

A knowledge of the behavior of two-phase, liquid-gas systems in equilibrium is of interest from many points of view. Particularly is this true when the behavior of such systems is determined over a wide range of pressures and temperatures. The limitations of such expressions as Henry's law and Poynting's rule are well known, and more general expressions are desirable. Simple two-component systems can be used and are of much scientific interest. Further, a study of two-component systems may form a basis for the consideration of more complex systems of equal scientific interest and greater practical interest.

The present work is concerned solely with systems formed of the simpler hydrocarbon gases and liquids. Such systems are useful in a scientific way in that the deviations from the simple ideal laws of solution become very great, and so are easily determined at relatively moderate pressures. On the practical side, investigations of such systems are useful in giving information as to conditions existing in the producing horizons of oil and gas fields. The primary reason for this work is, in fact, the study of conditions in the producing horizons of the Turner Valley oil and gas field of Southern Alberta. Because of this the systems studied were the first members of each hydrocarbon series and the actual products of the Turner Valley field. Further, such investigations as these have value in view of the trend to higher pressures in industrial practice during recent years. The information obtained may be of service in the design of processes and equipment.

Previous to the inception of this work, the literature covering the subject was relatively scanty. Most of the work dealt with only one of two phases in equilibrium, and further, the components were, in the chemical sense, quite unrelated. Some work on systems of natural gas and associated oils had

appeared (1, 4, 6, 8), and Frolich had determined the solubility of methane in various organic solvents (5) at pressures as high as 200 atm. The most comprehensive work on the subject appeared in recent years as a succession of papers by Sage, Lacey, and collaborators. The first of these papers (9) described apparatus and methods. Their methods differ greatly, in general, from those developed here, and, while their field of investigation is wider, little overlapping of results occurs.

The aim of the present investigations was to devise suitable apparatus and methods, and to determine the composition and density of both phases existing in equilibrium. Single phase systems were not considered; this limits the investigation to univariant equilibria shown as lines on two-dimensional phase diagrams. The pressure was varied from atmospheric to the critical value of complete miscibility or to a maximum of 370 atm. A temperature range of 25° to 125° C. was employed, and higher temperatures may be used when desirable. The gas used was substantially methane, and the liquids comprised a number of lower hydrocarbons of each series. Present work is concerned with a complex mixture such as occurs naturally in the Turner Valley oil and gas field of Southern Alberta. This report deals solely with methods and apparatus used in examining the simple systems.

Apparatus

The apparatus comprised in its essentials, means of compressing and storing gases, the equilibrium pipettes, and analytical apparatus. The information desired for simple systems was merely the composition and density of the gas and liquid phases in equilibrium. Consequently, it was not necessary to know precisely the amounts of liquid and gas added to the equilibrium pipettes. It was necessary only to be certain that two phases existed, and that the samples of liquid and gas withdrawn for analysis were homogeneous. These conditions were fulfilled easily at the lower pressures, where the amount of liquid added could be varied relatively widely without the disappearance of a phase. At high pressures, particularly near the critical value, the allowable variation in the amount of liquid added was very much less but still appreciable. None of this is true for complex systems. In such cases, both the amount of liquid and gas added must be known.

Compression and Storage of Gases

The gases used were prepared and purified at atmospheric pressure (3) and compressed into a 15 litre storage vessel. Two gases were used, both derived from Viking natural gas; one contained some ethane and nitrogen besides methane, and the other contained only nitrogen besides methane. From the 15 litre storage vessel, *A*, Fig. 1, the gas could be taken directly to the equilibrium pipette, or compressed further by hydraulic means, depending on the pressure desired. With valves 1 and 2 open, and valve 3 closed, the cylinder *B*, of five litres capacity, could be filled with gas. After valve 1 was closed and valve 3 was opened, the pressure of the gas could be raised to the desired value by means of the hydraulic pump shown. The pump was

fed with a 50% glycerine-water mixture. The pressure bottles D and E contained calcium chloride and activated coconut charcoal respectively. The tube F contained copper oxide heated to 320° C. and the pressure bottles G and H contained solid sodium hydroxide and calcium chloride. The five
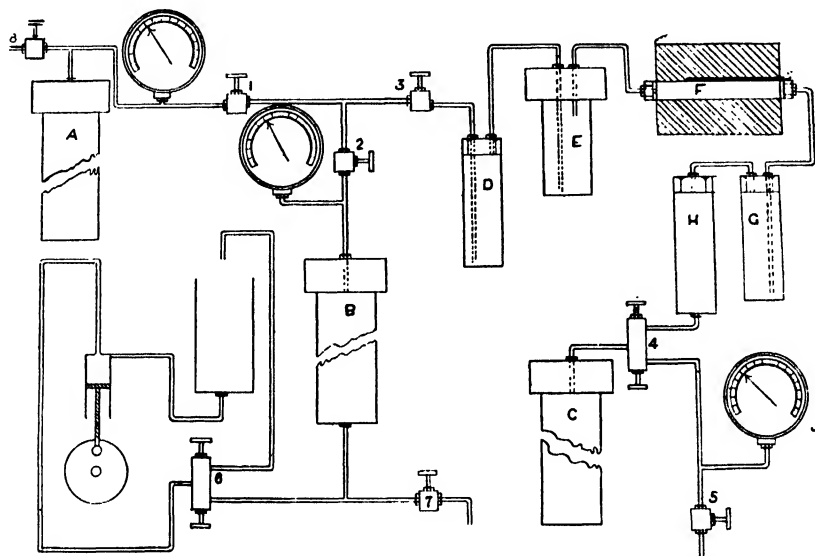
FIG. 1.   *High pressure storage, compression, and purification apparatus*

litre vessel C acted as a subsidiary storage for gas at the pressure obtaining in the equilibrium pipette. Provision was made for heating this cylinder, and thereby raising the gas pressure above that possible by use of the hydraulic cylinder. Connection was made through valves 4 and 5 to the equilibrium pipette as desired. The pressure gauge, J, was used to determine the pressure of gas in the equilibrium pipette. This gauge, of standard Bourdon type construction, was calibrated frequently against a dead weight piston gauge certificated by the National Physical Laboratory, England.

The Equilibrium Pipette

A conventional drawing of the apparatus is shown in Fig. 2. It was so designed and assembled that the gas and liquid phases reached equilibrium with each other at a reasonable rate, and known volumes of each phase could be withdrawn for analysis.

The sample of gas phase was obtained from the upper, or gas phase, pipette, A, and the sample of liquid phase was obtained from the lower, liquid phase pipette, B. These pipettes were in communication from their ends with the two central reservoirs as shown, and could be isolated by closing valves 2, 3, 4, and 5. The materials in these sampling pipettes could be withdrawn through valves 6 and 7 and led through tube E to the analytical apparatus.

The volume of the sampling pipettes was determined by weighing the amount of mercury required to fill them under pressure. The volume of the

gas phase pipette was 11.206 ± 0.005 cc. and that of the liquid phase pipette was 21.002 ± 0.005 cc. The volume of each central reservoir was 60 cc. approximately. The pipettes were calibrated at intervals, and showed no appreciable change in volume.
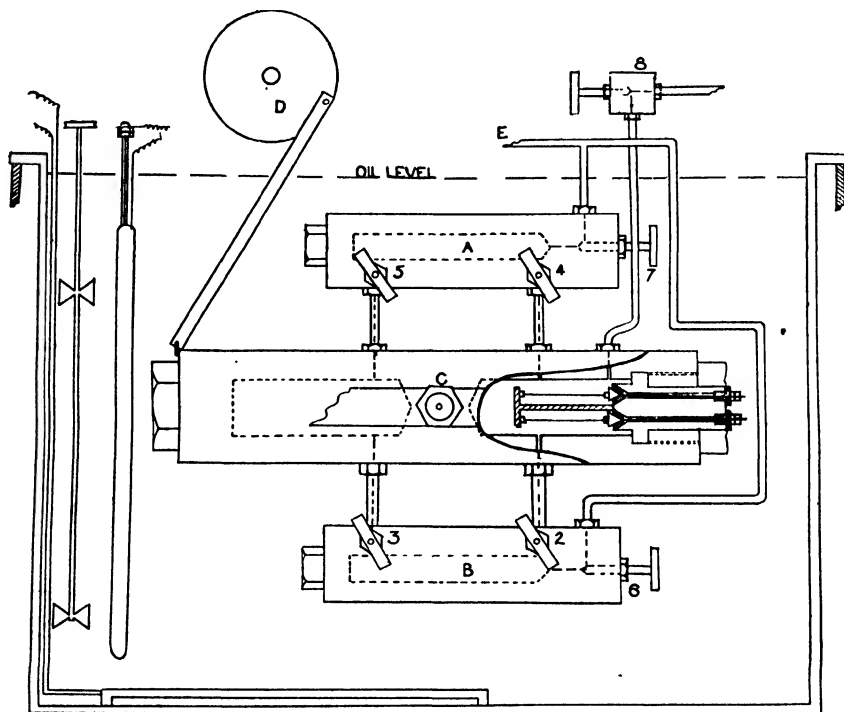
FIG. 2.   *High pressure solubility pipettes assembly.*

The whole assembly was pivoted at C and could be oscillated through 90° by means of a gear train and crank, D. The gear train was so equipped with cams and a clutch that the pipette assembly was held in each extreme tilted position for one-half minute during each oscillation. The tilting motion was sufficiently rapid to provide agitation of the contents of the central reservoirs. Holding the assembly in each extreme position for one-half minute permitted the flow of liquid from the higher central reservoir through the liquid phase pipette to the lower central reservoir, the gas phase moving at the same time through the upper pipette. At high pressures near the critical value when the density difference between phases was small, it was necessary to assist the flow of liquid and gas. A close-fitting steel piston, which fell by gravity from one end of the pipette to the other as the assembly oscillated, was placed in the lower pipette. Leakage past this piston, while not great, permitted sufficient circulation to ensure uniform composition throughout the liquid phase.

The approximate liquid level in the central reservoirs when horizontal was ascertained by means of the electrical indicator shown in the cut-away section in Fig. 2. The indicator depended for its operation on the different thermal

conductivities of the liquid and gas phases. Two identical platinum wires, 2 in. long, 0.0015 in. in diameter, within the reservoir served as two arms of a Wheatstone bridge. The leads, of heavy steel rods, from the external circuit were insulated and made gas tight by double compression cones of ebonite. A small constant current, 0.06 amp. was fed to the bridge and served to heat the wires slightly. A sensitive wall-type galvanometer served to indicate balance in the bridge. When the liquid level was between the platinum wires, the galvanometer showed a large deflection. If both wires were in the same phase, there was little or no deflection. Thus, the liquid level could be determined to within about $\frac{3}{8}$ in. of the central line through the reservoir, a determination sufficiently accurate for work with systems substantially two-component. It was necessary only to ensure that there was, at all times, two phases in the apparatus, and the boundary was in the central reservoir.

The temperature of the pipette assembly was maintained constant to within 0.1° C. by means of a thermostatically controlled oil bath shown. The bath was heated electrically and could easily be raised to a temperature of 125° C. The whole bath, heaters and thermostat included, was designed in such a manner that it could be lowered clear of the pipette assembly in order to permit manipulation of valves.

The Analytical Apparatus

The essential parts of the collecting and measuring apparatus for dealing with the expanded contents of the pipettes are shown in Fig. 3.
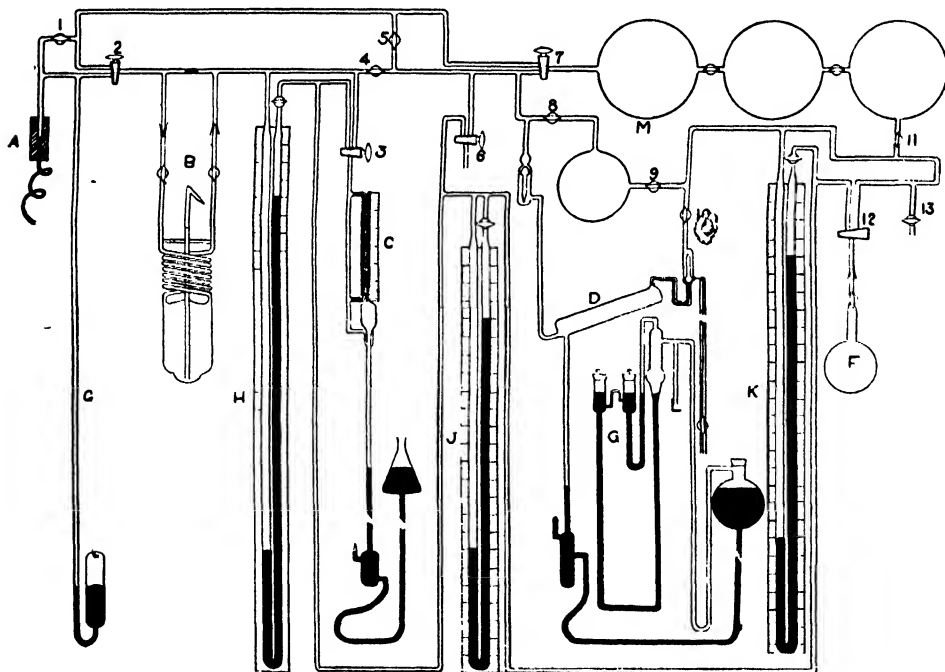
FIG. 3. *Expansion, separation, and measuring apparatus.*

Connection to the pipettes was made by means of a flexible copper tube ending in the glass-to-metal joint, A. A mercury sealed safety tube, G, protected the glass apparatus against accidental sudden liberation of the pipette contents. Pressures to the left of stopcock, H, were measured on manometer H or on the McLeod gauge C. A condenser, B, was attached, as shown, to the apparatus by ground glass joints, and could be removed for weighing. Other types of condensers, interchangeable with that shown, could be used when it was more convenient to do so. An automatic (7) Toepler pump, D, was used both as a circulating pump to mix the gases released from the pipettes, and to evacuate the pipettes; this ensured the removal of all the material in the pipette. The four bulbs, M, acted as a gas storage and measuring system in conjunction with the manometer K. The volume of each bulb was determined accurately, and the whole assembly surrounded by an air bath. No temperature control was used, the temperature in the bath being determined at the time of measurement by means of a calibrated thermometer within the bath. The volume of all tubing between stopcocks, 9, 10, 11, 13, and 12 was determined to a fixed high point on the left manometer arm. The volume of the manometer tube was also determined below this point. Three of the bulbs were of approximately two litres capacity, and the fourth, one litre. The volume of the tubing to the manometer was approximately 60 cc.

Samples of gas were taken through stopcock 12 to the half-litre bulb, F, of known volume for density determinations. The weight of bulb F was determined when evacuated and when full of gas in the usual manner, with a similar sealed bulb as counterpoise and calibrated weights. Samples of gas for combustion analysis were removed through stopcock 13.

Mercury diffusion pumps backed by an oil pump were connected to the apparatus through stopcock 6. These pumps were used in evacuation of the system prior to the releasing of the contents of the pipettes, and were used periodically to evacuate the right side of all manometers. The millimetre scales used with the manometers were calibrated periodically by comparison with a precision cathetometer.

Procedure

The pipette assembly, Fig. 2, was tested under pressure for leaks, evacuated, and flushed with gas from the storage system. A funnel was fitted to valve 8 and the correct amount of liquid, as found from experience, was added. With valves 6 and 7 closed, and valves 2, 3, 4, and 5 open, gas was admitted through valve 8 until the pressure was that desired. Valve 8 was closed, the oil bath raised into position, and oscillation of the assembly begun. After 15 min., connection was made to the gas supply, and the pressure adjusted to the desired value. This cycle of operation was repeated until no discernible pressure drop occurred in the pipettes after one hour of oscillation. The bath was lowered and valves 2, 3, 4, and 5 were closed. The contents of the sample pipettes were removed, the liquid sample first, through valves 6 and 7 in turn for analysis. In making a duplicate experiment, liquid to replace that

removed in the samples was introduced through E to the lower pipette, the appropriate valves adjusted and the procedure described above repeated. In this way the contents of the central reservoirs were not liberated.

The whole analytical apparatus, Fig. 3, up to the pipette connections, was evacuated. Stopcocks 1, 3, 5, 6, 7, 8, 12, 13, and 9 or 11, depending on the storage capacity desired, were closed, and 2 was opened to the pipette. A cooling mixture was placed around the condenser, B, and the valve on the pipette opened very slightly. The rate of expansion was such that about 100 cc. of gas per min. was liberated. When the pressure in the pipette had reached that of the analytical apparatus, the volume to the left of stopcock 7 was evacuated by means of the pump, D, to a pressure of about 4 mm. of mercury. The condenser was isolated and evacuation continued, with stopcocks 1 and 5 open, to a pressure less than 0.1 mm. of mercury. After stopcocks 1, 2, 4, and 5 were closed, the condenser was removed and weighed in order to obtain the weight of liquid recovered.

The gas, now in the bulbs, M, and the Toepler pump, was circulated for one-half hour or more by means of the pump until the composition was uniform. Stopcock 7 or 8, as the case might be, was closed, and the gas remaining back of the Toepler pump was passed into the bulbs, and the mercury level raised to stopcock 10, which was then closed. The pressure and temperature of the gas were measured, and density determinations made with the calibrated bulb, F. The volume of gas was calculated to N.T.P.

Samples of gas were passed through stopcock 13 to the combustion analysis apparatus. The gas always contained some small amount of the liquid hydrocarbon as vapor, and the amount was determined by combustion analysis, using a modification of the method of ultimate organic analysis for carbon and hydrogen (2). Combustion in the usual types of Orsat apparatus for gas analysis was not sufficiently precise to give the data required.

The data obtained as described above were sufficient to give the mass and composition of the contents of each sample pipette when the gas used contained only methane and nitrogen. The errors possible in the procedure were numerous but generally small. The pressures in the equilibrium pipette were reproducible to less than 10 lb. per sq. in., and the temperature was always constant to better than 0.1° C. The volume of the pipettes was known to about 0.04%, a variation that was negligible. The change in volume of the sample pipettes with pressure was calculated roughly to be 0.05% for the extreme range. Attempts were made to measure this change directly by filling the pipettes with mercury under different pressures. The change in volume with pressure as measured was less than the experimental error of 0.005 cc. Changing temperature had an appreciable effect on pipette volume. The increase in volume was calculated in every case and added to the volume found at 25° C. as a correction at higher temperatures.

The possibility of adsorption on the steel surface was eliminated by measurements of the volume of gas liberated at different pressures and with different areas of steel surface.

Errors in the method of analysis were relatively great and might reach 0.5% at the lower pressures used. At pressures greater than 1000 lb. per sq. in., however, this error was only one or two tenths of one per cent.

The chief errors appeared to arise in the equilibrium pipettes themselves. With a gas of two components, duplication of an experiment would require exactly the same amount of liquid and gas in the pipettes. This was only roughly true in this case. The increasing deviation between the results of experiments at the lower pressures may be attributed to the increasing relative error in pressure measurements. It did not appear possible to duplicate the conditions of equilibrium to better than 0.5% at the lower pressures or to about 0.2% at the higher pressures. Deviations between duplicates at the lower pressures reached, occasionally, 2%, particularly if a gas containing some ethane was used.

After the technique of operation had been systematized, it was possible to carry out an experiment in one day. A duplicate experiment required a second day and the calculations most of a third day.

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THE OXIDATION OF METHANE AT HIGH PRESSURES

I. PRELIMINARY EXPERIMENTS[1]

By E. H. Boomer[2] and J. W. Broughton[3]

Abstract

Mixtures of oxygen and methane at pressures from 100 to 180 atm. were passed at various temperatures between 300° and 350° C. over some catalysts. Simple apparatus was used and analytical technique developed. The production of methanol as an important product of oxidation, together with small quantities of formaldehyde and formic acid, was shown. Yields of these three products as high as 37% of the carbon oxidized were obtained.

Introduction

Oxidation is one of the most common and certainly, from the practical point of view, the most important of the few general reactions of paraffin hydrocarbons. Reaction with oxygen may be brought about under various conditions of temperature, pressure, concentration, and with catalysts. Because the reaction is general and is of scientific as well as great practical interest, it has been the subject of much study. The significance of such another study lies in its practical applications rather more than in its scientific importance. The Province of Alberta is heavily endowed with supplies of natural gas of which the major component is methane. The possible daily production is several times greater than the demand and a great deal of wastage occurs. Some process yielding useful liquid products from the surplus gas is, obviously, of interest.

The direct production of alcohols, aldehydes, or even acids by oxidation of paraffin hydrocarbons is a process offering obvious attractions. In the case of methane, two stages are necessary, at present, for the production of methanol; these involve conversion to carbon monoxide and hydrogen followed by a catalytic reaction under pressure. The problem has received considerable attention in the past, particularly at pressures near one atmosphere. It has been shown conclusively by Bone and collaborators (4), by Wheeler and Blair (15), and others, that oxygenated derivatives were formed in the reaction of oxygen with paraffin hydrocarbons at low pressures. The yields of alcohol, aldehyde, or acid were, however, very small. More recently, claims have been made (3, 9) of higher yields by the use of nitrogen oxides as gaseous catalysts. Another report of high yields at low temperatures and pressures with solid catalysts has also appeared (6). From a study of the results reported and much unsuccessful work here, the writers have been convinced that yields of useful products of practical interest cannot be obtained at low

pressures. Consequently, attention was turned to the use of pressure as a means of improving yields and suppressing undesirable reactions in the oxidation of methane.

The application of the "hydroxylation" theory proposed by Bone (4) to the process suggests clearly that an increase in pressure would result in more methanol and less of the succeeding products of oxidation. This has been confirmed amply by Newitt and Haffner (11), Pichler and Reder (14), by Newitt and Szego (12), and by Yoshikawa (17), as well as in the work carried out in these laboratories. The use of the "peroxide" theory (5, 7) does not appear to be necessary in considering the oxidation of methane. Norrish (13) offers an alternative to the "hydroxylation" theory and suggests the production of free radicals as the primary step followed by that of formaldehyde as the primary stable product. The usefulness of the theories of Bone and of Norrish in the present work may be taken as evidence of their essential correctness.

On the practical side, the work of Wiezevitch and Frolich (16) only need be considered. They oxidized, under pressure, various natural gases with oxygen, in contact with various catalysts, and determined optimum conditions for the production of useful products. They showed that yields were high only if the concentration of oxygen was low, and the yield of useful products on the basis of carbon input per pass was low. This paper includes an excellent bibliography on the subject.

Much of the published results of work at high pressures appeared after the inception of the work here and, it may be said, confirmed substantially the authors' findings. The work to be described in this and succeeding papers deals primarily with methane, but includes, as in the present report, work on a gas containing small amounts of ethane and propane. The production of methanol in high yields and with large conversion per pass of reactants was desired. This paper will discuss generally some preliminary work and give details of a few experiments in which copper and silver were used as catalysts.

Experimental

A number of experiments were performed in which a large steel reaction vessel was used. The reactor was used empty and also with a variety of oxide catalysts at temperatures ranging from 235° to 450° C. and pressures of about 200 atm. Natural gas alone was employed in some experiments to determine whether the oxides were reduced by the hydrocarbons under the conditions of temperature and pressure used. A second series of experiments employed oxygen-natural gas mixtures containing 7.3% of oxygen by volume. No appreciable yields of useful products were obtained in any case. The oxide catalysts, including barium peroxide, vanadium pentoxide, and blue tungstic oxide were relatively inactive. Two Hopcalite type (10) catalysts were prepared and used. They promoted oxidation violently for a short time and then became inactive. An interesting result was obtained with the empty steel reactor. Oxidation proceeded rapidly and to completion,

and gave carbon oxides and water. The steel surfaces were corroded severely and much iron oxide was formed. The steel was a high nickel-chromium variety and when used as catalyst in the form of turnings showed no corrosion.

The lowest temperatures at which oxidation became apparent varied with the catalysts. The Hopcalite catalysts promoted oxidation at temperatures as low as 125° C. but after the initial action was over, a temperature of 310° C. was required. Silver promoted initial oxidation at 200° C. and required a temperature of 300° C. or higher for rapid reaction. Copper, steel, and the other catalysts showed activity at 250° C. Copper promoted rapid reaction at 325° to 350° C. and the others required temperatures in excess of 375° C. Copper and silver were found to be superior to all other catalysts in the promotion of desirable reactions giving methanol.

Following this preliminary work, a tubular, copper-lined reactor was built and a series of experiments were carried out using metallic copper and silver as catalysts with oxygen-natural gas mixtures containing 7.3 to 7.5% of oxygen. This series of experiments was of interest and provided experience upon which later work was based. The results will be presented, in part, in what follows.

Materials

Viking natural gas was used in all experiments. This is a dry gas of high methane content and of the following composition: methane, 95.7; ethane, 1.4; propane, 0.9; nitrogen 2.0%. The gas contained organic sulphur compounds which were introduced as an odorant before distribution to consumers. These sulphur compounds were removed in a manner that will be described in connection with the apparatus. The oxygen employed was the commercial gas obtained from liquid air and compressed in steel cylinders.

Mixtures of the natural gas and oxygen were prepared by passing the two gases through meters simultaneously and in the desired proportions to a water-sealed gas holder. The mixture was dried over calcium chloride and compressed into a steel storage vessel. Oxygen concentrations higher than 7.5% were not used because of the danger of explosions.

The copper wall of the reactor was used as one of the two catalysts. The other catalyst, silver on asbestos fibre, was prepared by reduction of silver nitrate with concentrated formic acid in the presence of acid-washed, long-fibre asbestos. The silvered asbestos was washed and dried.

Apparatus

The apparatus is shown in conventional form in Fig. 1. The gas mixture entered the apparatus through valve *A*, and passed through 98% sulphuric acid in the scrubber, *B*, which was filled with broken glass. The sulphuric acid completely destroyed the organic sulphur compounds, probably by oxidation (2), and the sulphur was converted to sulphur dioxide. The steel bottle *C* contained solid potassium hydroxide, which removed the sulphur dioxide and water. In bottle *D* activated coconut charcoal served to give the gas mixture a final purification. A recording Bourdon type gauge, *E*, gave

a record of the pressure throughout a run. The reaction tube, F, was placed vertically in the furnace, H. A heavy copper lining, G, between the furnace heaters and reactor served to aid in uniform temperature distribution. The volume of the reaction space in the reaction tube was approximately 7.5 cc. Temperatures were recorded and controlled automatically by means of an
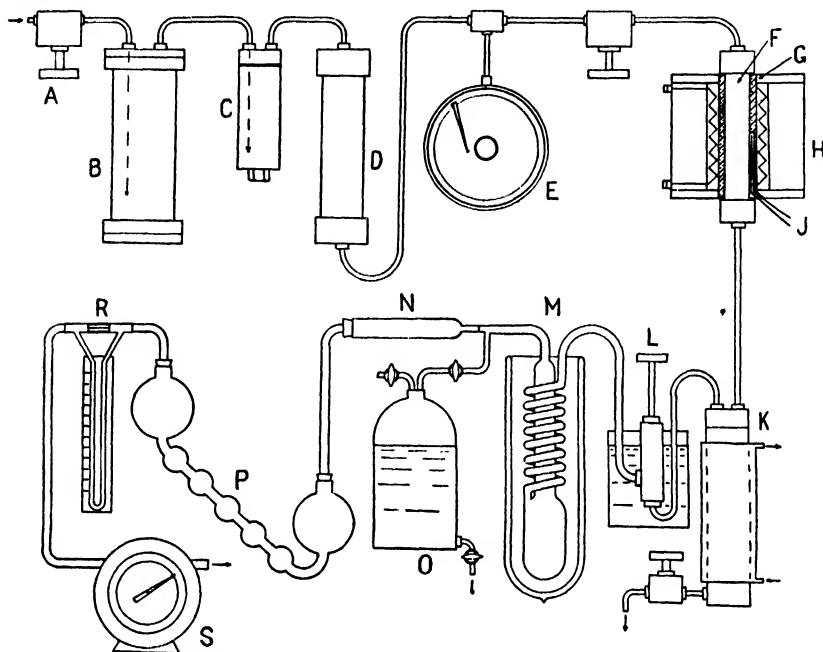
FIG. 1. *High pressure purification and reaction apparatus with low pressure recovery apparatus.*

automatic potentiometer and the thermocouple, J. Liquid products of the reaction were collected in the water-cooled high pressure condenser, K. In order to reduce corrosion, this condenser was chromium plated on the inside, and the connections to the reactor and expansion valve, L, were of heavy walled copper tube. The expansion valve, L, was capable of fine control of the gas flow and was maintained at a temperature of 100° C. by means of an oil bath. The expanded gas passed through the glass condenser, M, which was cooled in an ice-bath, then through a calcium chloride tube, N, to collect water vapor, and the water scrubber, P, to collect traces of formaldehyde that escaped condensation. A constant rate gas sampler, O, was used to take a continuous proportional sample of the off-gas. The rate of gas flow was shown by the flowmeter, R, and the quantity of off-gas measured with a test meter, S.

Analytical Methods

The liquid products in the high pressure condenser were blown into the ice-cooled glass condenser at the end of a run, and the weight was determined. The gain in weight of the calcium chloride tube was also determined. The

liquid products, together with the contents of the water scrubber, were made up to 100 cc. in a volumetric flask and measured portions were taken for analysis. The only method suitable for methyl alcohol determination was found to be that of Fischer and Schmidt (8). The method depends on the quantitative formation of methyl nitrite and its subsequent hydrolysis to methanol and nitrous acid by hydrochloric acid in the presence of potassium iodide. The liberated iodine is titrated with sodium thiosulphate. The method, with slight modifications in procedure, was found very satisfactory and precise. Certain identification of the alcohol present was obtained by preparation of the 3,5-dinitrobenzoic acid ester derivative, m.p. 106.8° C. A mixed melting point determination carried out with a laboratory reagent product and the ester prepared from the condensate gave the same value. Ethyl alcohol was also present in very small amounts as shown by the iodoform reaction. The ethyl alcohol may be attributed to the presence of ethane in the gas.

Formaldehyde was determined by Romijn's cyanide method using a modification of the procedure (1, p. 261) capable of high accuracy. Volhard's method of cyanide determination was used.

Formic acid was determined by warming a sample of condensate to drive off carbon dioxide, adding an excess of standard sodium hydroxide to decompose any salts or esters present, and back-titrating with standard acid. Copper salts were frequently present and copper hydroxide was precipitated with excess alkali. This was filtered off before back-titration with acid.

The gain in weight of the calcium chloride tube was taken as water. Analyses carried out on the contents of the calcium chloride tube showed less than 0.5% of the total methanol as having escaped the condensers. This quantity was within the experimental error in the procedure. Confirmation of the quantity of alcohol in the condensate was obtained frequently by fractional distillation in a vacuum jacketed column.

The analysis of both in-gas and off-gas was carried out with an improved Bureau of Mines Orsat apparatus. No measurement of the volume of in-gas was possible, but calculations based on the amount and composition of the off-gas and liquid products could be made. Carbon was used as the reference element in the calculation of material balances. Oxygen was not satisfactory because of an unexplained loss in most runs. This loss of oxygen will be referred to again.

Results and Discussion

The results of a number of runs with the copper lining of the reaction tube as catalyst and for two runs with silver catalyst filling the reaction tube are given in Table I. A considerable number of data have been omitted from the table, the principal figures being those giving the ratio of the volume of in-gas to off-gas. This figure was remarkably constant at 1.10, within the limits of error, in experiments in which the oxygen was all, or nearly all consumed. This is, of course, what might be expected; variations do occur but they are small. The ratio of the amount of oxygen passed in to that

TABLE I

THE OXIDATION OF NATURAL GAS UNDER VARIED CONDITIONS OF TEMPERATURE,
PRESSURE, AND RATE OF FLOW

Experiment No.	24	26	27	28	29	30	34	45	46
Catalyst	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Ag	Ag
Temp., °C.	325	325	325	350	350	350	350	310	312
Pressure, atm.	183	161	119	117	109	95	117	173	153
Off-gas flow, litres per min.	0.80	0.58	0.9	0.9	2.0	2.0	0.9	2.0	3.82
In-gas, oxygen, % by volume	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.5	7.5
Off-gas, % by volume									
CO_2	2.3	2.9	1.4	2.6	2.0	2.5	2.3	1.4	1.7
O_2	1.4	1.7	3.4	0.5	0.4	0.1	0.6	0.1	1.0
H_2	0.4	0.3	0.3	0.5	0.5	0.4	0.4	0.4	0.5
CO	0.6	0.8	0.7	1.4	1.9	2.0	1.5	1.6	2.3
CH_4	84.8	88.6	86.8	89.5	88.1	86.8	—	89.1	90.1
C_2H_6	2.4	0.0	0.0	0.0	0.5	1.4	—	0.0	0.0
% of total carbon oxidized	4.40	4.95	2.93	5.65	5.94	6.30	5.88	4.40	4.85
Yields, as % of carbon oxidized to,									
Methanol	35.9	25.3	27.1	30.2	34.2	29.7	31.8	31.5	17.9
Formaldehyde	0.8	1.0	1.0	1.2	0.9	1.7	2.1	1.7	1.4
Formic acid	0.0	0.0	0.0	0.4	0.3	0.1	3.2	0.6	0.4
Total	36.7	26.3	28.1	31.8	35.4	31.5	37.1	33.8	19.7
Concentration of methanol in condensate, wt. %	38.7	31.2	36.2	33.0	36.7	40.6	33.8	24.4	19.8

emerging, as found in all products has been omitted. This ratio was less than 1, generally, and varied erratically. The loss of oxygen has not been accounted for, and in later work, to be published, definite attempts were made to find the source of the discrepancy. The phenomenon is not new and has been reported elsewhere (16), also without explanation.

From 5 to more than 10 cu. ft. of gas, measured at N.T.P., was used in each experiment and the weight of condensate varied between 2 and 3 gm. per cu. ft.

While many duplicate experiments were made, only one pair has been included in the results given. Experiments Nos. 28 and 34 were selected as being typical duplicates. It will be seen on inspection that the results are substantially the same in each case, excepting only in formic acid production. The variations shown were usually found with duplicate runs and have been attributed to temperature changes. The reactions are highly exothermic and precise temperature control was impossible, even though automatic control was supplemented by manual control. Variations of as much as 10° C. from the temperatures tabled existed occasionally for a few minutes in most runs.

The runs given in Table I are sufficient to show, at least qualitatively, the effect of the several variables on yields. Considering Nos. 27 and 28, carried

out at substantially the same pressures and rates of flow, it is evident that the yield of useful products has been more than doubled by a 25° C. rise in temperature. At the rate of flow used, little more than half of the oxygen was used at 325° C. This accounts for the low consumption of carbon. The efficiency of the process measured by the fraction of carbon oxidized and entering into the formation of useful products was slightly greater at the higher temperature. With temperatures lower than 325° C. reaction was very slow and methanol production small. At higher temperatures, above 350° C., oxidation proceeded very rapidly, and the methanol yield fell off above 375° C. even at high rates of flow.

The effect of pressure is generally evident at both temperatures when the different rates of flow are taken into account. From a comparison of Nos. 24 and 27, it is seen that a decrease in pressure results in lower carbon consumption and a lower efficiency in the conversion of carbon to compounds. The change is too great to be attributed to the slight increase in rate of gas flow. From a consideration of No. 26, together with the other experiments, the effect of rate of flow is evident. The reduced rate of flow resulted in a greater carbon consumption, but the efficiency of production of compounds was decreased greatly. The efficiency is very much less than that found at the higher pressure and rate in No. 24, but is also less than that found at a lower pressure and higher rate of flow shown in No. 27.

Generally, a study of both series of experiments shows the effect of changing pressures and rates of flow. Within the limits used, increasing pressure gives greater carbon consumption and higher conversion to compounds. The effect of changing rate of flow appears to be more complicated. At low rates, carbon consumption is high, but the conversion to useful products is low because of more complete oxidation resulting in formation of carbon oxides and water. As the rate of flow is increased, other things being equal, carbon consumption is decreased, but the efficiency of conversion to compounds increased. Obviously, with the practical criterion, conversion of total carbon to useful compounds, as a measure, there is an optimum rate of flow at which the two opposing factors give a maximum production of methanol. For the present apparatus, at 100 atm. and 350° C., it would appear that the optimum rate of flow is at least two litres per minute measured as off-gas.

The results with the silver catalyst, Nos. 45 and 46, are interesting, particularly in showing the greater activity of silver in causing rapid reaction at low temperatures. The decreased production of methanol in spite of a higher consumption of carbon in the second experiment is unexpected. More of the carbon appeared as carbon oxides, particularly carbon monoxide. This would suggest that the equilibrium between methanol and its decompsoition products, carbon monoxide and hydrogen, plays a part in the process occurring in the reaction tube. Alternatively, it should be pointed out that the reaction temperature may have been very much higher in the second experiment because of the poor heat conductivity of the catalyst.

While the silver catalyst cannot be compared, except roughly, with the copper catalyst because of differences in physical form, it is of interest to discuss their different actions. The copper catalyst always contained oxygen, probably in the form of cuprous oxide. Starting with a fresh pure copper surface, reaction resulted in pitting and a change in color to that of cuprous oxide. On the other hand, the silver catalyst was reduced and did not show any traces of silver oxide. That silver differed from copper in its actions was also shown by the production of methyl formate. Over copper, only traces of the ester were ever found while with silver, most of the formic acid appeared as methyl formate. This result may of course be attributed to the asbestos support used, a more probable catalyst for esterification. It should be pointed out finally that the temperature given, representing that of the reactor wall, may differ greatly from the temperature of the silver catalyst because of the poor heat conductivity of asbestos and the exothermic nature of the reactions.

It was expected that the higher hydrocarbons would be oxidized most easily and be absent from the off-gas. This was generally true, but exceptions occurred that could not be attributed to experimental error. Later work showed the possibility that higher hydrocarbons were synthesized in the process. The subject will receive further consideration in another report.

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IMPROVED PACKED FRACTIONATING COLUMNS[1]

By D. F. STEDMAN[2]

Abstract

The factors limiting the utility of packings for fractionating columns are considered in detail. In view of these factors a type of packing is described which gives an effectiveness up to 20 plates per foot of height, and has a capacity at least equal to similar equipment of lower efficiency.

These packings are constructed of fine mesh wire gauze, and special constructions are described for laboratory use and also for high capacity apparatus.

The method of calibration is given and factors are evaluated for comparison of packings for batch and for continuous stills.

In work under consideration several years ago the need for a type of fractionating column of higher efficiency than types generally available was felt very seriously, and since preliminary experiments showed that very considerable improvement was possible, an attempt was made to find a really effective construction with the desired properties.

There are in general two types of column, the bubble tower and packed columns of various sorts. The former has proved very satisfactory for continuous fractionation, but for batch processes its large liquid tie-up is a decided disadvantage, while the packed type is of general utility. In this study it was also felt that such an enormous amount of work had been done on bubble plates under such a wide variety of direction, which had in fact achieved a very notable improvement, especially in capacity, over earliest types, and that further improvement along these lines was therefore improbable. In view of the fact that only minor changes had been found useful, despite very widespread commercial use and investigation, and that present plate efficiencies range from 50 to 85%, it would seem that this type of equipment is probably operating very close to its optimum. Further improvement must therefore come from some type of film contact, rather than from the dispersion of either phase in the other.

In a fractionating column the primary process of separation is the passage of constituents from the vapor through the interface to the liquid, and from the liquid through the same interface to the vapor. Now, in apparatus in general use for such fractionation, the relative velocity between the liquid and vapor at any particular point is quite small, a few feet per second. It is therefore evident that stagnant films of very appreciable thickness will be present on both sides of the interface, *i.e.*, there is a stagnant "boundary layer" of both liquid and vapor forming a partition at the interface through which the constituents must pass by diffusion processes. In any attempt to increase the effectiveness of fractionation apparatus, it is therefore of importance to consider the nature and speed of this diffusion process in order to make the best use of it.

If k_m is the mean diffusion coefficient through the entire boundary layer of thickness S, and area A, and W the weight of ascending vapor, the change in composition which can be brought about in the vapor composition in unit time is

$$\frac{k_m A}{S W} \Delta X \ , \tag{1}$$

where ΔX is the deviation from equilibrium compositions from liquid to vapor.

In this expression k_m and W are fixed for any particular application, and, therefore, only A, S, and ΔX can be varied. Of these A can be varied directly but not without some correlation with other factors, such as liquid hold-up, while ΔX can vary only from 0 to the equivalent of one theoretical plate, and S can be controlled by indirect methods only.

Thus in the design of fractionating equipment of the liquid-vapor equilibrium type, only the following modifications can improve their efficiency:—

A. Increase in the contact area between liquid and vapor phases.

B. Increase in the time of contact of the two phases.

C. Improvement of the "natural mixing coefficient" of the body of liquid and vapor by so shaping the parts that the work available for the production of turbulence is utilized in the best manner.

D. Increase in column heights, so that more work may be available for production of turbulence in the liquid phase.

E. Increase in the back pressure on the column so that more work may be available for production of turbulence in the vapor.

F. Addition of mechanical work to increase turbulence, by means of moving elements.

G. Distribution of the available work between the two phases so that they are both mixed at "equivalent" speeds, and work is not wasted in mixing one phase too much and the other too little.

H. The design of the column so as to secure more even distribution of both liquid and vapor across the column section.

In general consideration of the utility and limitations of these methods of improvement, it is obvious that A directly increases the effectiveness, but it must be noted that such increase in the contact area is generally accompanied by an increase in the liquid tie-up, which if directly proportional is not beneficial in batch distillation.

In general B can be accomplished only by increasing the volume of the column which is not desirable. C is obviously advantageous, as far as it can be carried, but both D and E are definitely undesirable for many reasons, and in fact the main purpose of the present and similar work is to effect a reduction in these items.

Unless definitely beneficial results can be obtained by F which cannot be achieved otherwise, this seems to add a distinct complication to the apparatus, which if possible should be avoided. G is obviously desirable, but it is rather difficult to evaluate how far any particular construction deviates from the ideal in this respect, while H is entirely advantageous, but can be carried only to the point of uniformity.

Thus the items of design which can be examined to secure improvement, other than mechanical moving parts, are: (1) to obtain as large a contact area as possible, while keeping the liquid tie-up at a minimum; (ii) to shape the parts to obtain good mixing in both phases; (iii) to distribute the mixing between the phases to give equivalent and suitable mixing to both, and (iv) to design the column to secure even distribution of both phases across the column section.

After these items have received attention, the question of the use of added mechanical power to increase either the capacity or effectiveness of the column can be considered.

General Consideration of Factors Involved in Packed Columns

As turbulence, or bulk mixing, and diffusion, or molecular mixing, play such important roles in these phenomena, it is useful here to note the physical properties of the types of liquids and vapors concerned in the processes, and check over the general considerations involved in an attempt to find the factors limiting the effectiveness of present equipment.

Table I gives approximate values for the densities, diffusion constants, and viscosities, showing the range in which most liquids and vapors fall. Little work has been done on diffusion at elevated temperatures and consequently

TABLE I

AVERAGE VALUES FOR CERTAIN PROPERTIES OF LIQUIDS AND VAPORS

Density, D, of liquid at b.p.	0.5	1.5
Density, d, of vapor at b.p.	0.001	0.005
Diffusion constant of liquid, K, cm²/sec. at 20° C.	5×10^{-6}	2.5×10^{-6}
Diffusion constant of vapor, k, cm²/sec. at 20° C.	0.1	0.05
Viscosity of liquid at b.p.	0.002	0.004
Viscosity of vapor at b.p.	0.001	0.0002
$\sqrt{K/k} \cdot D/d$	3.5	2.1
$\sqrt{k/K}$	0.007	0.007

the values have been taken from data at 20° C. As no effort is made in this paper to obtain great accuracy in these calculations, these values will be adequate for present consideration if allowance is made in an approximate manner for the effect of higher temperatures.

Useful Film Thicknesses in Both Phases

Let F be the thickness of the boundary layer on the surface of the liquid, and f the thickness of the similar layer in the vapor; also let Δx be the change in composition from the interfacial liquid to the body of the liquid, and $\Delta'x$ the change in composition from the interfacial vapor to the body of vapor.

If the notation indicated in Table I is used, the weight of substance diffusing from the body of the liquid to the interface through area A in time t is

$$\frac{AtDK(\Delta x)}{F} ,$$

while the similar quantity for the vapor is

$$\frac{Atdk(\Delta'x)}{f} ,$$

which quantities are equal (on the assumption that the latent heats for the constituents being separated are equal).

Therefore,

$$\frac{F}{f} = \frac{DK(\Delta x)}{dk(\Delta'x)} . \tag{2}$$

Now the film in the vapor is set up by the material passing through the interface from the liquid, and conversely the film on the liquid side of the interface is formed from material from the vapor. Consequently, if a portion of vapor is suddenly placed in contact with liquid at the same temperature, but with which it is not in equilibrium, the amounts of the liquid and vapor constituents passing each way will be equal, and as a first approximation

$$DF(\Delta x) = df(\Delta'x) . \tag{3}$$

Owing to the shape of the diffusion waves set up this is not exactly correct, but is quite adequate for obtaining an insight into the fundamental factors involved.

Substitution of the value of x from Equation (3) in Equation (2) gives

$$\frac{F^2}{f^2} = \frac{K}{k} \text{ , or } \frac{F}{f} = \sqrt{\frac{K}{k}} \tag{4}$$

and the liquid film is therefore

$$\frac{FD}{fd} = \sqrt{\frac{K}{k}} \cdot \frac{D}{d} \tag{5}$$

times heavier than the vapor film.

The values of film thicknesses for the usual range of liquids and vapors have been calculated from Equations (4) and (5), and are given in Table I, from which it will be seen that the useful film of liquid weighs two to three times as much as the similar vapor film, and from the value of $\sqrt{k/K}$ is about 140 times thinner.

Flow Conditions, or Turbulence in the Vapor

It is also necessary to consider the state of turbulence of the phases, and as an example the turbulence conditions for vapor rising with a velocity of 30 cm. per sec. in tubes 1 cm. diam. might be calculated, using mean properties from Table I. Reynolds number (velocity × diameter × density ÷ viscosity) under these conditions is 500. As the critical value for a straight tube is 2000, such flow would be streamline. However, for conditions other than a straight smooth tube the critical value is lower, and for a circular tube with a single partition, provided with a central hole, faint turbulence is obtained at a Reynolds number of 250, and is very decided at 500. If further partitions across the main tube are added the first sign of turbulence naturally builds up as each partition is passed. However, as the flow pattern past such a partition is quite smooth and laminar at a Reynolds number of 200, it is to be expected that additional partitions would then have no effect. Such a tube, with many partitions, is evidently very similar to a very much bent path such as obtains in the vapor passages of a packed column.

From the above it is evident that with vapor velocities of 30 cm. per sec. in tortuous passages 4 mm. or less in diameter, streamline flow is obtained with most vapors at room temperature, and at higher temperatures even larger openings would still give laminar flow, as the density is decreased by heating and the viscosity increased.

The importance of turbulence in the vapor may be noted by the following simple calculation. Consider a column filled with 4 mm. tubes, and assume that no resistance is offered to diffusion by the liquid films, and calculate the amount of interchange by diffusion into the non-turbulent vapor stream, assumed to be rising at a rate of 30 cm. per sec. If a mean value for the diffusion constant be substituted in Equation (1), using an approximate path length of 2 mm., it will be seen that about 0.4 cc. of vapor will diffuse for each square centimetre of contact area per second. Since 30 cc. of vapor passes upwards per second, this gives a rate of doing fractionation work of 0.4/30 theoretical plates for each square centimetre of contact area per square centimetre of column section, or it would require 75 sq. cm. of contact area per square centimetre of column section to give one theoretical plate, if perfect distribution of both phases is assumed.

Now, short lengths of 4 mm. tubes, 4 mm. long, packed irregularly give 4.7 sq. cm. of contact area per cubic centimetre, so that such a column, with perfect distribution of both phases and streamline vapor flow would need 16 cm. per theoretical plate. Thus without turbulence even such fine packing as 4 mm. tubes, used under ideal conditions as to liquid distribution, which certainly cannot be realized in practice, gives hardly two plates per foot of height.

If, however, the flow were turbulent the concentration gradients at the interface would be much higher, and large increases in ·efficiency might be expected if the liquid could be distributed in such thin uniform films that the original assumption is approached.

Flow Conditions in the Liquid Phase

It is also desirable to consider the most suitable speeds at which the reflux liquid should be mixed in order to prevent the accumulation of products absorbed from the vapor in the surface of the liquid. Suppose the column contains n times as much liquid as vapor, any mutual transfer of material affects the liquid composition n times less than it does the vapor, and consequently mixing must take place n times more frequently in the liquid in order to change the composition of the bulk of liquid as rapidly as that of the vapor.

Now the minimum height in which the vapor must be mixed is one theoretical plate, so that if $n = 40$, a very common value, and it is hoped to achieve 10 theoretical plates per foot of height, the liquid must be mixed at least 400 times per foot, or the surface film, at least, must be "turned in" 33 times per inch of height to achieve this result, and if any lack of uniformity exists in the distribution of either phase, whereby efficiency will be lost, the liquid must be mixed even more rapidly.

Comparison of Existing Columns with the Above Requirements

In applying the above considerations to the usual types of packing it is evident that in most cases the turbulent conditions are reasonably well fulfilled in the vapor phase, although there is little doubt that with some laboratory packings made from very small objects the vapor flow is in the main streamline. However, the very frequent subdivision of the vapor stream is somewhat equivalent to turbulence and there is little doubt that many packings rely entirely on this effect.

With respect to rapidity and uniformity of mixing in the liquid phase, many packings evidently could be improved considerably, as quite large drops of liquid collect between parts of the packing and descend bodily in a random manner. There is also obviously room for improvement in many cases in the bulk distribution of both phases, *i.e.*, avoiding channeling; and also in the micro-distribution, *i.e.*, ensuring that every portion of liquid and vapor acts respectively in the same manner at the same speed throughout the column, and many packings could be improved very much in respect to the production of thin uniform liquid films, which are obviously desirable both for reducing liquid tie-up, and for obtaining good contact with the vapor.

Application of These Considerations to Actual Packing

In order to obtain as rapid and continuous mixing of the liquid as possible, it seemed that if the surface over which the liquid flowed were made very rough this might help the process. It was also desired to use an orderly arrangement rather than to rely on "the uniformity of complete disorder", and obtain as large an area of interface as possible with the least amount of liquid. As a material to satisfy all of these requirements, wire gauze seemed to offer interesting possibilities, which it was felt had not been explored at all completely.

Wire mesh has been used fairly extensively in fractionating columns, but experiments on such material as fly screen showed that although it may be built into a packing in a regular manner, it acts in an essentially random manner, *i.e.*, drops and streams of liquid collect and pass downwards in random positions governed by surface tension and the chance irregularities in the material while very little of the reflux is properly distributed. Tests on different meshes, however, showed that if quite fine gauze is used continuous films are produced and the process is quite different, in that the material floods all over and the flow of liquid can be definitely controlled by the shape of the structure over which it flows, without that extreme sensitivity to microscopic irregularities so noticeable with the coarser meshes.

It was found that about the most satisfactory mesh sizes were from 56 to 60 warp wires per inch and from 36 to 40 shute wires, using about 10 mil wire. It will be seen that the wire is quite heavy for the mesh, and is in fact as heavy as can be woven, in order to increase the roughness of the surface as much as possible. This size gives a capillary rise of 18 to 22 mm. with most organic solvents at room temperature if shaken with the solvent in a closed tube, and this effect evidently contributes considerably to the uniformity of flow of the liquid.

There now remains the question of the type of pattern to be used in forming packing from such material, and in this connection the latest and generally most satisfactory form will be described first, with the reasons for adopting it.

In Fig. 1 is shown diagrammatically a comparison between bad types of packing and good. Fig. 1, *A*, represents a vertical curtain of fairly coarse mesh, while Fig. 1, *B*, represents an edge view of an inverted V of fine mesh. The paths of liquid and vapor are indicated, and it will be seen that both diagrams are similar in this respect, with, however, the fundamental distinction that in *A* the liquid path is controlled entirely by chance irregularities and the flow of vapor, the liquid avoiding the vapor as much as possible; while in *B* the distribution of liquid is essentially independent of the vapor. At high vapor velocities the turbulence of the vapor will naturally disturb the smooth flow of the liquid, form ripples, etc., but on the average both

FIG. 1. *Comparison of bad (A) with good (B) types of liquid and vapor flow.*

limbs of the V will be equally affected. Thus *A* illustrates a cumulative effect, and if the structure is continuous complete segregation of both liquid and vapor will result, with a minimum of intermingling, while with *B* slight unavoidable irregularities will cause one side of the V to receive more liquid than the other, but as the vapor no longer controls this ratio the effect is not cumulative, and on the average a uniform and stable distribution of liquid is produced.

Thus with the construction shown in Fig. 1, *B*, the primary subdivision of the liquid takes place at the apex of the V, and is, what might be termed, a structural subdivision, which is not affected either by the amount of vapor that happens to be passing upwards through this point in the packing, or by the fraction of this vapor that passes out of either side of the V. Conversely the above considerations also apply to the vapor flow, and this type of construction, therefore, removes the interaction of liquid and vapor and provides no mechanism by which channeling can be initiated.

In Fig. 2, *A*, is shown a plan and elevation of a single cellular element shaped to make use of the principle of Fig. 1, *B*. It will be seen that it is simply a cubical or rhomboidal box standing vertically on one corner. The lowest corner is truncated to provide an entrance for vapor, and exits are provided at the other three lowest corners. Thus liquid poured on to the apex of the cell will be divided into three streams, one on each face, and the rising vapor will be subdivided similarly, each process being independent of the motions of the other phase.

Cells of this type might appear rather complex to use as column packing, but they are actually produced in a basically simple manner.

FIG. 2. *A. Single gauze cell. B. Sheet of gauze.*

Sheets of gauze are perforated with a series of equidistant holes, and are stamped into a pyramidal pattern. This pattern is indicated in Fig. 2, *B*, where the point *Y* is intended as a raised triangular pyramid, and each hole (henceforward to be referred to as *O*) is at the bottom of a pyramidal indentation. These sheets are then stacked together, the next sheet being placed in the same orientation above that indicated in the figure, but with a lateral shift, point *Y* being over point, *O*. The sheets are then spot-welded into position and the process repeated. This builds up a continuous lattice of cellular elements exactly similar to Fig. 2, *A*, the only difficulty being the fact that rather complex presses are required to produce the stamped sheets of gauze.

No diagram of the completed structure is given as it is almost impossible to make such a diagram in an illuminating manner, and the path taken by the liquid and vapor is perhaps best seen by considering the passage through each element. It will be seen that there is a cell directly beneath points *A, B*, and *C*, Fig. 2, *B*, and if the next sheet is added there will be a cell directly over *O*. Thus the opening *O* is fed with vapor equally from each of the cells under *A, B*, and *C*. and this vapor after passing through the cell above *O* is again divided into three streams as it passes upwards through the next layer of cells.

It will also be seen that each edge of each cell throughout the packing is a junction line for four plane surfaces of gauze, two of these planes supply liquid to the junction line, and, after the two films of liquid are partially mixed at the junction line, this liquid is redistributed over the two lower planes. It is therefore evident that with this constant mixing and redistribution of both phases no appreciable deviation from uniformity can exist, either in the amount passing through or the composition of either phase from point to point in any horizontal level in the column.

Mention might be made of the necessity of providing drainage at the bottom of this packing. It is self-evident that if the liquid is simply allowed to fall from the lowest points of the bottom sheet, the edges of the vapor holes, the hanging drops of liquid will lose all capillary effect and be blown about freely by the rising vapor. The capacity of the column will then be limited entirely by this effect, and will not be more than about half its normal value. This is prevented by attaching narrow depending strips of gauze about $\frac{5}{8}$ in. long, one for each vapor perforation, as shown in the lower part of Fig. 3. These maintain capillarity till the liquid is well below the vapor opening and allow the full capacity of the packing to be utilized. Other methods of drainage may also be used, but this is the method usually adopted for laboratory packings.
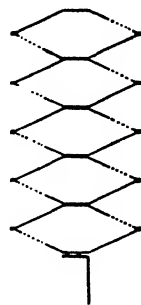
Fig. 3. *Conical pattern.*

This type of packing, termed the "hexagonal" pattern, has been made in sizes up to 6 in. diameter, and larger sizes are now under development, but for laboratory uses an even more effective type of packing has been developed. This is illustrated in Fig. 3, and consists of a series of gauze discs pressed into truncated cones and welded alternately base to base, and edge to edge. Each disc has a vapor perforation at one side as indicated by the dotted line, and the vapor, after passing through each cell by means of these openings, passes between the containing tube and the gauze round both sides of the axis before passing to the next cell.

It will be seen that the liquid is alternately brought together at the base of each cone and spread in a film over the broad portion of each surface, this action preventing variation in composition from point to point in the liquid. The vapor is also treated somewhat similarly in that it passes in a single turbulent stream through each cell, and then divides into two streams, passing behind and in front of the packing. In this case, mixing is somewhat less important, as each phase passes through the packing in practically one stream.

It will be seen that this type uses a rather longer path of contact than the "hexagonal" packing shown in Fig. 2; this gives it a greater height effectiveness, but at the same time decreases its capacity. These factors can be controlled quite readily by the depth of pressing, and the size of vapor opening,

but naturally capacity can be increased only at the expense of effectiveness, or *vice versa*.   As at present made in 1 in. tubes the proportions are chosen to give 20 cc. of hexane per min. capacity at total reflux.

Calibration Procedure

Many attempts were made to calibrate columns two or three feet long, but this was ultimately abandoned as the results were often very misleading, and it has been found most satisfactory to calibrate quite short lengths, of not more than five theoretical plates.   For this purpose a mixture of very highly purified *n*- and cyclo-hexanes is used containing about 25% of the former.   A diagram of the column and stillhead arrangement is given in Fig. 4, and the procedure used is as follows:—

The boiler is electrically heated and the watts supplied measured, the heater wires being in contact with the flask as an aid in preventing "pumping".   The whole flask and heater are buried in rock wool, while the column is wrapped in soft asbestos cord to keep heat losses uniform and small.   The heat necessary to raise the vapor level just to the base of the packing is determined, and subtracted from the watts used in all experiments.   As the columns are invariably quite small and the hexane very volatile,

FIG. 4.   *Calibration still-head.*

further insulation or actual heating of the column is not necessary.   The vapor composition is calculated from the composition of liquid in the still (on the assumption of 1.2 theoretical plates of separation), and the latent heat of this vapor is taken by a weighted mean from 30,160 J for cyclohexane and 28,600 J per mol for *n*-hexane.   Vapor velocities are then calculated from the watts used and this mean latent heat.   This calculated vapor composition is however not used in the calculation of the effectiveness of the columns.

Temperatures were originally measured with a platinum resistance thermometer, but as this temperature determines only when the column has reached equilibrium, a standard time of 20 min. boiling has been adopted as this has been found quite adequate for these columns when used in this manner, and an ordinary thermometer is now used as a check on the general operation.

The condensed liquid passes over a small reservoir, 1 cc. volume, blocked by a mercury seal, and after equilibrium is established the mercury is lowered and raised again rapidly, the small sample being caught in a cooled tube to prevent vapor loss from the hot liquid.

As the concentration of *n*-hexane in the pot is quite appreciable, about 25% in 200 cc. of liquid, the composition of the liquid in the pot at any time is obtained from its original composition.   This is possible as the tie-up of liquid in the column is very small and small corrections only are required.

Corrections are, therefore, made to the original composition for:

1. Vapor loss during the initial heating of the flask, using the volume of air exhausted and the condenser temperature, and on the assumption that four theoretical plates of separation were involved. This figure was obtained by means of thermometer readings, and as a result the loss is largely *n*-hexane, but is usually only about 0.3 cc.

2. Liquid in the column and condenser. This is measured with petroleum ether at room temperature, in order to simulate the surface tension effects obtaining during normal use of the apparatus with hot liquids. Thus the ether is added (through a long tipped burette) to nearly the bottom end of the water jacket through the condenser at a definite rate till it drips from the packing, and the volume used is noted. The process is repeated at different speeds.

3. Continuous loss to the atmosphere while running the still.

4. Loss of each sample during examination and while returning it to the still.

This seems rather a complicated procedure, but it obviates the handling of two lots of samples with a resulting greater loss of material, and expedites the actual calibration procedure, at the expense of a little calculation. All these corrections are, however, quite small; thus No. 2 involves only 3 to 4 cc. of liquid in the usual test, and the actual losses are even smaller. The total consequently affects the result very little.

The cyclohexane, which was purified by distillation of c.p. grade, has a freezing point apparently 0.17° higher than is reported for the Bureau des Etalons standard material. This freezing point was measured with a thermometer freshly calibrated by the Reichsanstalt, but as this sample was not compared directly with the standard material this freezing point is cited simply as showing that the cyclohexane was of satisfactory purity for this procedure. The *n*-hexane was the best sample obtained during tests on hexanes which will be described elsewhere, and contained a few hundredths of 1% of both methyl cyclopentane and 3-methyl pentane. Separation of these traces of impurities will be entirely negligible when such small quantities are used in columns only a few inches high.

The packing used was from 2 to 6 in. high and was adjusted so that the concentration of *n*-hexane did not become too near 100%, generally not over 80%, and the separation coefficient (α) taken as 1.433 as a mean over the range from 25% to 75% *n*-hexane. Ideal solutions are assumed and the equations solved mathematically, rather than graphically.

Analysis of samples is made by either refractive index or apparent boiling point, or both, and both procedures have been standardized by means of mixtures of the actual samples subsequently used in the still.

In Table II is given a typical set of results obtained during calibration of a short length of the hexagonal packing with ⅜ in. cells, at one low speed, a fairly high speed, and the flooding limit. These measurements are taken at total reflux for a series of speeds covering the entire range possible for the particular packing.

TABLE II

CALIBRATION OF 2 IN. OF ⅜ IN. HEXAGONAL PACKING (19 SHEETS OF GAUZE)

	A	B	C
Total watts supplied to still	49	256	290.5
Corrected mol. percentage of *n*-hexane in pot at time sample taken	29.4	28.3	27.9
Corrected mol. percentage of cyclohexane in pot at time sample taken	70.6	71.7	72.1
Mol. percentage *n*-hexane in product at total reflux	75.5	56.3	58.5
Mol. percentage cyclohexane in product at total reflux	24.5	43.7	41.5
Calcd. theoretical plates (assuming $\alpha = 1.433$, and ideal solutions)	5.61	3.32	3.62
Plates correction by calibration without column (interpolated from plot) at same watts	2.55	1.20	1.19
Plates in column	3.06	2.12	2.43
Theoretical plates per foot height	18.36	12.72	14.58
Cc. per minute at bottom of column	7.1	56.0	64.2
Cc. per minute at top of column	5.9	56.8	65.6

NOTE:—*Column cross section, 1.096 sq. in.*
Original mol. percentage of n-hexane in pot, 30.1%.
Original mol. percentage of cyclohexane in pot, 69.9%.
Watts required to raise vapor line to bottom of packing, 19.
Watts required to raise vapor line to top of packing, 26.

In some cases the packing is then removed from the column and the still and empty column recalibrated in order to determine the efficiency with no packing, but in all final measurements a dummy column is substituted which, while similar to the actual column, is shortened by the length originally occupied by the packing. This shortened and empty dummy then corrects for any "end effects", without including a length of empty column as is involved in the more approximate method of removing the packing. The results are then calculated to theoretical plates with and without the packed section of column, and the difference in plates per foot of height is plotted against the speed of reflux in cubic centimetres per minute per square inch of column section.

Effectiveness Obtained with These Packings

A series of results showing the calibration of various types of packing made from fine mesh gauze is plotted in Fig. 5. The patterns used in these packings are:—

(1) Horizontal prismatic cells, of ¼ in. square section; as these are not as effective they have not been described in detail.

(2) The same as (1) but using 0.18 in. square cells.

(3) Cones of 105° included angle and discs in 1 in. tube.

(4) "Hexagonal" pattern as in Fig. 2, $\frac{7}{16}$ in. cells indented to 30° slope.

(5) As (4), ⅜ in. cells, indented to give cubical cells.

(6) As (5), 1½ in. cells, $\frac{7}{16}$ in. perforations.

(7) As (5), 1½ in. cells, $\frac{13}{16}$ in. perforations.

(8) Conical pattern of Fig. 3, in 1 in. diam. tube.

The short vertical line at the end of each curve indicates the limiting speed at the flooding point, although No. 1 was not taken as far as this point.

It will be seen that these columns all give higher effectiveness at lower vapor speeds. This is perhaps partly due to the longer time of contact, but is no doubt partly produced by the gauze surface itself. Thus at lower reflux speeds it is correspondingly "drier", and the roughness of the surface is therefore more effective. The liquid is also present in thinner films, and therefore reaches equilibrium more rapidly.
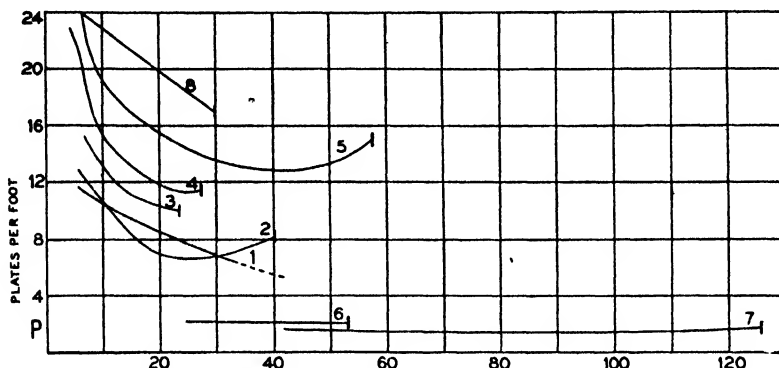
Fig. 5. *Plates per foot : reflux, cc./sq. in./min.*

This is in sharp contrast with the usual effect, which is either to show no change with speed, or in many cases a reduction of effectiveness at low vapor speeds. There is little doubt that the reduction often noted is due to the fact that channeling is taking place, and at low reflux speeds the liquid is not distributed properly, but passes downwards almost exclusively in the channeled streams. As channeling is not present in these columns, they are able to take advantage of the longer time of contact at slow speeds and thereby give considerably increased effectiveness.

Packings (1) and (2) give an interesting comparison, in that although (2) has 1.4 times the exposed surface of (1), it is actually less effective over a considerable range of speeds. This is evidently due to inadequate turbulence in the finer packing as these are of identical pattern except for the scale.

Packing (3) is somewhat similar to that shown in Fig. 3, but instead of pairs of cones, this pattern is made of truncated cones closed at the top with flat discs, two notches being cut in the edge of each disc for passage of vapor.

It will also be noted that Packing (8), Fig. 3, gives the greatest height effectiveness, but is limited in capacity, while (5) gives the greatest effectiveness at fairly high speeds, and (7) gives the greatest capacity, at of course reduced height effectiveness. Packings (5) and (7) can be modified to give a continuous series of effects intermediate between these two curves, or even higher capacity can be secured by increasing the size of the pattern beyond the size of (7).

Liquid Tie-up in Gauze Packings

Another item of considerable importance in column operation is the liquid retained in the packing. Owing, however, to the very small amount retained by these columns it is a matter of some difficulty to make such a measurement while operating, and consequently the dynamic liquid tie-up has been measured for comparison purposes with benzene at room temperatures.

The values needed for correcting the composition of the mixture in the still during calibration were obtained by running petroleum ether (30° to 60°C.) through the column and measuring the volume retained. This is done in order to simulate the lower surface tension obtained at higher temperatures, but this procedure is not accurate enough for exact comparison. Benzene was therefore run through the packing at a definite speed for a few minutes, and the stream interrupted simultaneously at top and bottom and the whole weighed to give the amount of benzene retained.

Fig. 6 gives a plot of the results obtained with the same series of columns, expressed in grams of benzene retained per square inch of column section 1 ft. high.
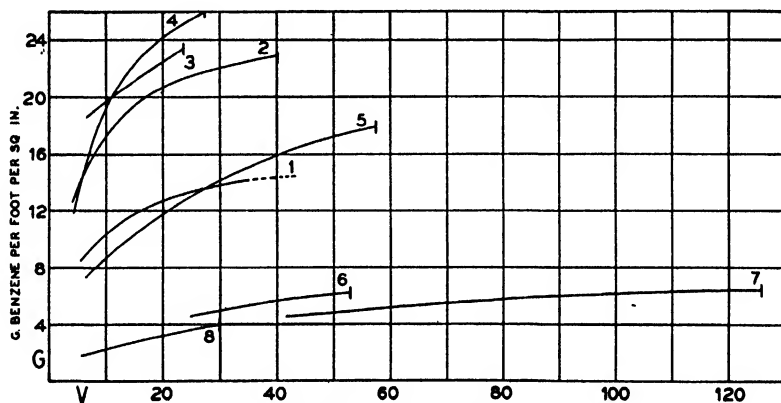
FIG. 6.   *Liquid hold up: reflux, cc./sq. in./min.*

It will be noted that Packing (3) is bad in one respect, in that the liquid retained does not decrease much at reduced speeds. This is obviously due to the use of flat sheets, which do not drain well, as part of the construction. The fact that (4) is so much worse than (5) is due to a similar effect; although no flat sheets are used in (4), the angle of the packing was not steep enough to give as good drainage as (5). The other packings give values as might be expected in comparison with each other. (6), (7), and (8) are low owing to their open structure, while (5) is higher as it contains more gauze per unit volume.

It will be noted that these values are the dynamic hold-up for liquid at room temperature which differs appreciably from the amount retained when operating and heated. Thus examination of these packings in use in glass tubes shows that considerably less liquid than the plots indicate is retained over the lower speeds, corresponding to the falling portion of the curves in Fig. 5, while quite near the flooding point the amount increases rapidly.

Derived Factors for Evaluating Packings

In order to consider the utility of any packing it is necessary to combine the data of Figs. 5 and 6 in some manner, and consequently the following derived factors are introduced as indicating the specific utility of each packing for particular purposes. If the data of Fig. 5 is considered as values of $P : V$ and Fig. 6 as $G : V$, a value showing the specific utility of each packing for use in batch stills is obtained

$$\frac{G}{P} \times \frac{60}{V} = W \, ,$$

and W, therefore, gives the weight of benzene retained in a column of diameter such that it will reflux at 1 cc. per sec. and of one theoretical plate effectiveness, when operated at all values of V possible with that packing. W is therefore directly proportional to the amount of material represented in the cut-off between a standard pair of liquids when tested with each packing at the speed (V value) chosen, and should of course be as low as possible.

The values of W, plotted against V as before, are given in Fig. 7, and it will be seen that Packing (8) is very much the best at all speeds permissible, while (5) and (7) are best in the higher speeds.
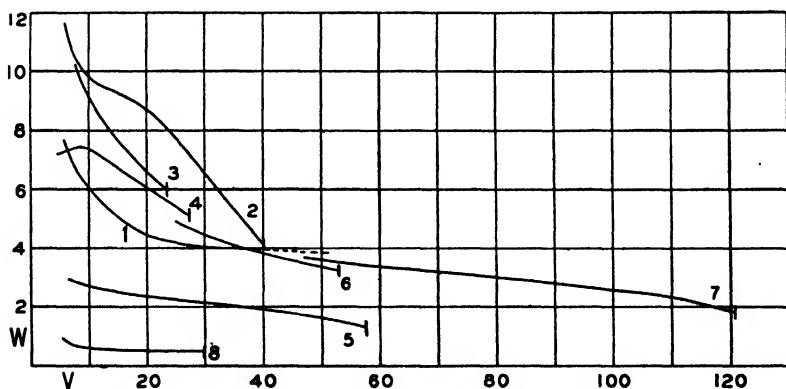
FIG. 7.   *W factor : reflux, cc./sq. in./min.*

Another factor is of importance for comparison of packings for use in continuous stills. If the same notation is used,

$$\frac{V \times P}{60} = C$$

and it will be seen that C represents cubic centimetres per square inch per second × plates per foot, and is a volumetric capacity factor expressed in distillation work units, and should be as high as possible.

These values are given in Fig. 8, and it will be seen that Packings (8) and (5) are the best, and while (7) appears somewhat disappointing on this basis, it must be noted that this packing has hardly one-quarter as much gauze per cubic foot as the others, and is therefore much cheaper to make. ✦
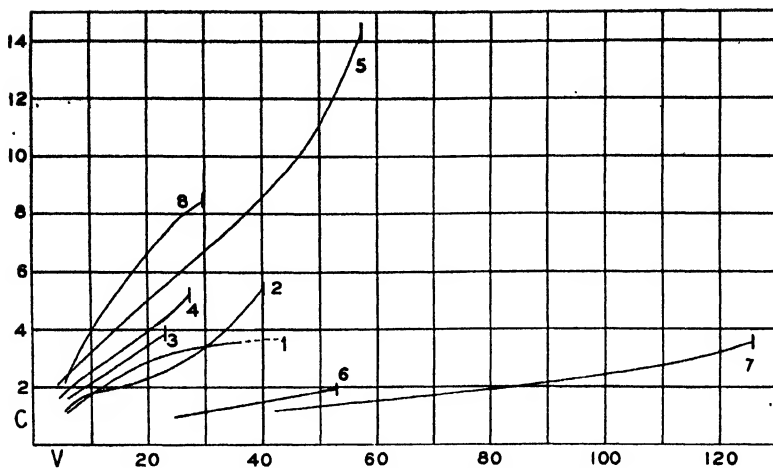
FIG. 8.   *C factor : reflux, cc./sq. in./min.*

In order to permit comparison of the amount of work obtained per sheet of gauze, the *C* values of Fig. 8 were divided by the number of sheets of gauze per foot of height; this gave values for an economic factor *E*. These are plotted in Fig. 9, where it will be seen that on this basis (7) reaches values slightly higher than any other.
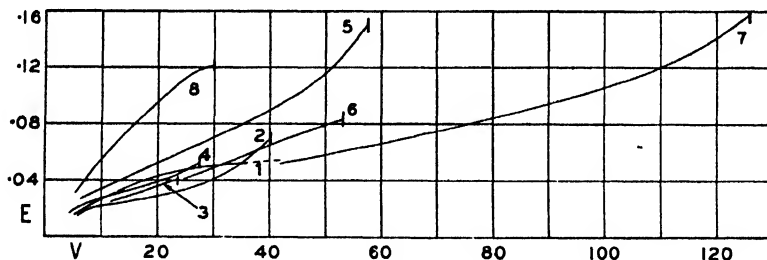
FIG. 9.   *E factor : reflux, cc./sq. in./min.*

Comparison with Other Columns Available

In general, fractionating columns show a very wide range of properties corresponding to widely different classes of use, but Table III gives a rough comparison of about the range generally available, although this list is of course not intended as complete, but is simply a selection of the better known types. The values for the capacity and effectiveness of these columns are also calculated to the corresponding *W* and *C* values for comparison with the gauze packing, although it should be noted that the micro-laboratory type is not actually available in the capacity listed, as its sectional area is very small. They are all, however, compared on the same basis, of capacity per square inch.

It will be seen that the *W* values range from 0.48 for gauze packing (8) up to over 100, while Packing (8) is on this basis nearly four times better

TABLE III
COMPARISON OF VARIOUS COLUMNS

Type of column	Plates per foot, P	Liquid tie-up, G	Capacity, cc./sq.in./min., V	W	C
Small laboratory columns					
a. Micro-type	3	4	45	1.78	2.25
b. Indented tube type	1	5	40	7.5	0.67
c. Packed type	(to) 4	50	30	25	2.00
Commercial "fine chemical" columns	0.75	45	35	103	0.44
Crude oil columns	0.3	40	100	80	0.50
No. 8	16.7	4	30	0.48	8.32
No. 7	1.7	6.5	125	1.81	3.59
No. 5	14.9	17.9	57.5	1.25	14.3

than the micro type. It has also a much larger reflux capacity, and is very suitable for treating small volumes of liquid in much the same manner as a micro-fractionation.

Gauze packing (5), it will also be seen, has a very low W value, and is therefore very suitable for use in batch stills, while as it also has a very high C value, exceeding in this respect all others in the list, it is excellent for use in continuous stills.

Applications of Gauze Packings

The utility of Packing (8) for laboratory purposes of all sorts is obvious; it has a C factor much higher than is given by the usual packings, combined with the lowest W value, and while in this size it is limited to about 20 cc. of reflux per min. this capacity is adequate for many purposes. For purposes requiring a higher speed, Packing (5) gives very good results. This pattern has been made in sizes up to 3 in. diameter, in which size it will carry about 400 cc. of reflux per min. It also gives excellent height effectiveness and has a fairly low W value. For still higher capacities Packing (7) is the most suitable, it has a much lower height effectiveness, but for columns of large diameter this is not detrimental as it keeps the ratio of height to diameter at a reasonable figure, while the smaller patterns give such short lengths of packing that distribution of reflux over a large section becomes difficult. One of the main advantages of changing the size of the pattern is in fact to secure a column of suitable proportions.

One special use might also be noted for Packing (3), and any other pattern including horizontal sheets in its construction. These patterns are very useful for the treatment of mixtures which give two liquid phases, as the phase which does not wet the gauze is trapped on the horizontal surfaces, while patterns using only sloping elements allow this phase to "skate" over the continuous film formed by the other phase and pass downwards too rapidly for proper fractionation.

One further advantage of this type of construction* might also be noted, in that the actual weight of the packing is very small in comparison with such apparatus as bubble towers, etc., and consequently for use with corrosive materials a smaller quantity of the expensive alloys sometimes needed will produce a column of the required effectiveness and capacity. Thus in many cases, materials which may be prohibitive in cost if used in ordinary columns may be utilized in these gauze packings. For instance if Packing (7) is made of pure silver it would require 1 lb. of metal, per theoretical plate of effectiveness, per gallon per min. reflux; or a still equivalent to 20 theoretical plates for 10,000 gal. of reflux per day requires about 140 lbs. of silver in the gauze itself. At present prices this quantity of silver is worth about $750. The stainless steels are, of course, very suitable for many purposes, and in fact any alloy which can be drawn to wires may be used in these gauze packings for special purposes.

Experiments made with these packings and apparatus used with them will be described in later articles.

Patents: U.S. 2,047,444, and in other principal countries.

THE OXIDATION OF METHANE AT HIGH PRESSURES

II. EXPERIMENTS WITH VARIOUS MIXTURES OF VIKING NATURAL GAS AND AIR[1]

BY E. H. BOOMER[2] AND VICTOR THOMAS[3]

Abstract

Mixtures of a natural gas, substantially methane, and air in various proportions were passed over catalysts, and the effects of the variables, composition of mixture, pressure, temperature, and space velocity, were determined. Similar experiments were made with mixtures of methane and air. Mixtures containing from less than 3% to more than 13% of oxygen as air were used. The temperature range was 350° to 500° C. and the pressure range 140 to 230 atm. Methanol was the principal product, and yields as high as 74% on the basis of carbon oxidized were obtained. Copper was the principal catalyst used. Traces of sulphur poisoned the catalyst very effectively.

Introduction

In a previous report (2) some preliminary investigations on the direct oxidation of natural gas of high methane content under pressure were described. The present report gives results obtained in a systematic investigation of the subject in which natural gas from the Viking field and air as the source of oxygen were used. Massive copper, shown previously (2) to be an effective promoter of the reactions, was used exclusively in the experiments as a catalyst. The effects of composition of the gas mixture, the temperature of the reaction, the pressure, and the rate of flow of gas through the reactor were determined. ·

Equipment was designed and built which permitted more exact control of the variables affecting the reaction than was possible with the original equipment. The method used in this work resolved itself into bringing separately the gas and air in the desired proportions to a mixer immediately preceding the reactor, passing the mixed gas through the reactor to a high pressure condenser, and then through an expansion valve. After expansion, the off-gases were stripped of condensable materials, samples were taken for analysis, and their volumes measured.

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    [3] Demonstrator, Department of Chemistry, University of Alberta, 1934-1935.

Experimental

Materials

Natural gas from the Viking field, east of Edmonton, Alberta, was used throughout. Its composition was reasonably constant at 90.8% methane, 3.5% ethane, and 5% nitrogen by volume, as obtained by means of the improved Bureau of Mines type of Orsat apparatus. Actually, the gas contained propane in small amounts and the analysis is merely conventional. Such analyses, in the present work, serve to reveal the total carbon content of the gas, which is the element of interest. The gas also contained small amounts of the vapors of organic sulphur compounds added as an odorant. The sulphur was removed completely in the apparatus to be described.

Air was used as a source of oxygen and was dried by passage over calcium chloride before compression. Carbon dioxide was removed from the compressed air, and a further drying carried out by passage over solid potassium hydroxide.

Pieces of electrolytic copper, $\frac{3}{16}$ in. square and $\frac{3}{32}$ in. thick, were used as catalyst. The weight of copper used was 39.8 gm. and its actual volume was 4.46 cc. The effective volume of the catalyst including free spaces was approximately 12 cc. The copper was activated by alternate oxidation and reduction prior to use. Air was used as an oxidizing agent and a mixture of hydrogen and methanol vapor as a reducing agent. This catalyst was very sensitive to poisoning by sulphur and the vapors of heavy hydrocarbons. The activity of the catalyst was restored either by activation as described above, or by immersion in dilute nitric acid for a short time. Copper in the form described was used in virtue of the good heat conductivity obtained. With exothermic reactions such as were investigated, the control of temperature becomes difficult if not impossible unless provision is made for rapid dissipation of heat.

Apparatus and Procedure

The compressed air and natural gas were stored in cylinders of such capacity that the pressure drop during an experiment would be relatively small, approximately 2 to 3 atm. The gas was stored at the pressure desired in the experiment, and the air was stored at a pressure some 35 atm. higher. The gas passed through concentrated sulphuric acid, solid potassium hydroxide, and activated charcoal to the reactor system, as described previously (2); thus sulphur was eliminated. The air was passed through solid potassium hydroxide before it entered the reactor system. Both lines included a check valve in front of the control valves on the reactor system to prevent accidental entry of air into the natural gas system.

The apparatus used to study the oxidation reactions is shown conventionally in Fig. 1. The gas and air were admitted through valves 1 and 2, both of which were so designed as to be capable of very fine adjustment. They were also equipped with electric heaters. The valve connected to the air supply was heated in order to counteract the cooling effect of a 35 atm. pressure drop and so maintain a constant rate of flow. The gas and air met in the mixer *A*.

The central hole of the mixer contained a snugly fitting piston, B, which had a shallow spiral groove cut along its length. The bottom of the piston fitted a ground seat in the mixer and acted as a check valve against explosions in the reactor; thus additional protection against mixing of the contents of the storage cylinders was obtained. From the mixer, A, a sample of the gas
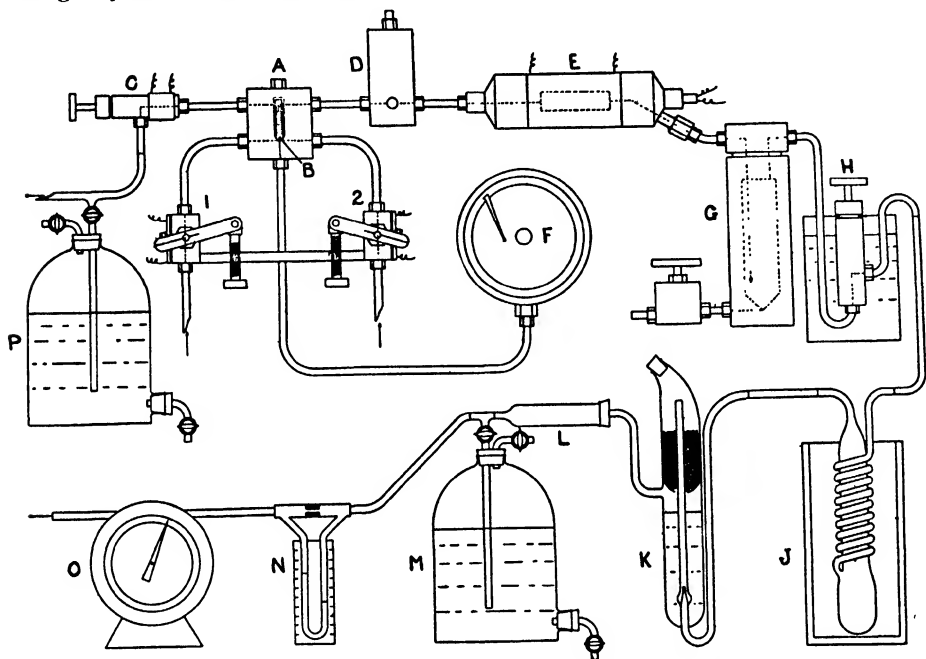
FIG. 1.   *Diagram of high pressure oxidation apparatus.*

mixture was removed continuously through the heated expansion valve, C. A record of the pressure during an experiment was obtained by means of a Bourdon Tube type recording gauge, F. This gauge was calibrated at intervals by means of a dead-weight piston gauge. From the mixer, the gas passed through a short tube to the reactor, E. A spring controlled relief valve, D, in the line was set to open at 50 atm. above the operating pressure.

The reactor, E, is shown in detail in Fig. 2. The body, B, was constructed of high nickel-chromium steel, and was heated electrically as shown. All other parts were cut from chrome-molybdenum steel bar. The inlet tube, A,
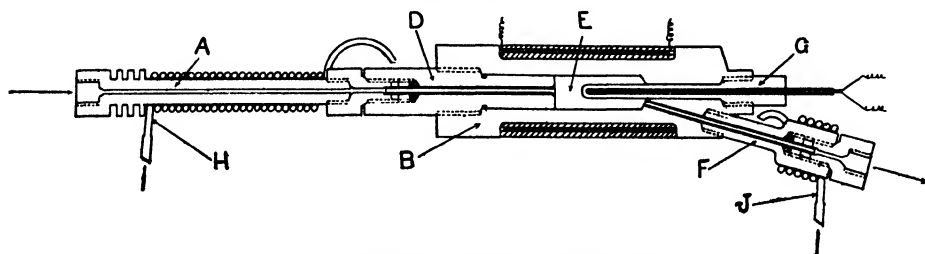
FIG. 2   *Diagram of high pressure reactor.*

and closure, D, were cooled by running water in the tube H; the outlet tube, F, was similarly cooled by water in the tube J. Both the closure, D, and outlet tube, F, were fitted with a lining of $\frac{1}{8}$ in. copper tubing, and all the interior surfaces of the reactor were copper plated. The temperature in the interior of the reactor was obtained by means of a thermocouple fitting the well, G. The temperature was measured on a recording potentiometer which controlled the power input to the heater, and maintained the temperature constant to within $2°$ C. The catalyst was placed in the space, E, of volume 12.7 cc.

From the reactor, the products of reaction passed through copper tubing to the chromium plated, high pressure, condenser, G, Fig. 1, the uncondensed gases passing on to the heated expansion valve, H. From the point of entry of the gases to the reactor closure, the gases and products were not allowed to come in contact with ferrous metals.

After expansion, the gaseous products passed through the ice-cooled condenser, J, the water scrubber, K, the calcium chloride tube, L, the' flow meter, N, and the wet-test meter, O. A continuous, proportional sample of the off-gases was taken throughout an experiment by means of the sampler shown in part as M.

The composition of the inlet gas mixture was controlled by continuous analysis, in a thermal conductivity cell, of the sample expanded through valve, C. At the same time, a continuous proportional sample was collected in bottle P. The thermal conductivity analysis apparatus was of the usual type. Two cells of about 3.5 cc. volume were cut in a copper block and fitted with identical coils of 0.0015 in. platinum wire, heated by a constant current. The wires formed two arms of a Wheatstone bridge. Pure dry air was passed at a constant rate of 10 cc. per min. through one cell, and the air-gas mixture was passed through the other cell at the same rate. The setting of the Wheatstone bridge to give balance was used as a measure of the composition. The instrument was calibrated by using known gas-air mixtures, and it readily showed a variation in composition of 0.2%. Previous to an experiment, the bridge was set for the desired composition. The gas valve, 1, was opened and then the air valve, 2, Fig. 1, was opened carefully and adjusted until the bridge galvanometer showed no deflection. Adjustment was continued throughout an experiment according to the movements of the galvanometer index. The lag between the time of mixing at B and the time the expanded gas mixture entered the analyses apparatus was about one minute. This method of nearly instantaneous, continuous analysis and control of the air-gas mixture was highly satisfactory.

The rate of flow of gas through the reactor was controlled by adjustment of the expansion valve, H. This valve, of non-ferrous materials, was constructed and fitted so as to be capable of fine adjustment and of staying in adjustment. It was necessary to keep the bath temperature fairly constant at $90°$ C. or higher to prevent erratic variations in rate of flow.

The procedure, after an experiment, has been described (2). Both the average in-gas and off-gas samples in bottles P and M were analyzed by conventional methods. The liquid products were collected and aliquot parts taken for determination of methanol, formaldehyde, formic acid, and occasionally, other constituents. As a check on the accuracy of the analytical methods, ultimate analyses were carried out occasionally for carbon and hydrogen. The standard method of carbon and hydrogen determination by combustion was used for the liquid condensate. Precise ultimate analysis of the gas was carried out by a method already described (3), the principles of ultimate organic analysis being used. The calculated amounts of carbon and hydrogen based upon the analysis for individual constituents were more than 98% of the values found by ultimate analysis. This left no doubt as to the accuracy of the analytical methods, and showed that the quantity of carbon compounds other than those tested for was negligible.

Results and Discussion

The results are given in the form of tables of data, and general features are illustrated by graphs. No experimental means was available for determining the actual volume of the in-gas, and an indirect method was used. The method consisted of the calculation of the weight of all the carbon in the products of the reaction, and, with the analysis of the in-gas, the volume ratio of in-gas to off-gas could be found. The method assumes, of course, that all the carbon entering the system was accounted for in the products. Every precaution was taken to ensure that this was true. In all the experiments tabled, except one noted, no carbon or compounds of carbon were deposited in the high pressure system. The analyses were all carried out in duplicate and checks obtained. Further, as described previously, the analytical methods were confirmed by ultimate analysis for carbon and hydrogen. Nevertheless some doubt arises as to the correctness of the results. On the basis of a carbon balance, the other three elements involved, nitrogen, hydrogen, and oxygen, did not show a good balance except rarely. The discrepancy in the nitrogen and hydrogen balances was commonly small, but it frequently exceeded experimental error. Generally, duplicate experiments agreed with each other, and no explanation can be offered for the discrepancies. The oxygen balances showed very great errors, sometimes positive but mostly negative. The errors were far beyond any experimental error conceivable. Many attempts to trace the oxygen discrepancy were made without any success. Among other tests, measurements of the volume of in-gas were made directly by pressure drop in the storage cylinder. While not very accurate, the agreement with the calculated volume was within the limits of error. The oxygen discrepancy was traced almost certainly to the reactor and catalyst, but no explanation was found. The phenomenon is not new and was reported by Wiezevitch and Frolich (5), also with no explanation.

Ignition Temperature and Explosions

Some preliminary experiments with high oxygen concentration made to determine the ignition temperature are given in Table I. Temperatures of 250° and 300° C. did not produce any reaction, but at 350° C., as in experiment

TABLE I

PRELIMINARY EXPERIMENTS AT 350° C. AND HIGH OXYGEN CONCENTRATIONS

Experiment No.	49	50	51	52
Pressure in atm.	147	150	150	199
Off-gas flow, litres per min.	0.80	0.51	0.84	0.84
In-gas analysis				
O_2	14.9	14.9	15.0	14.8
CH_4	26.2	26.2	26.7	26.6
C_2H_6	0.87	0.87	0.85	0.88
N_2	58.03	58.03	57.45	57.72
Off-gas analysis				
CO_2	1.4	3.0	2.81	3.9
O_2	1.46	2.2	0.75	0.80
H_2	2.1	1.1	1.44	2.60
CO	3.0	3.8	4.02	4.40
CH_4	23.1	24.4	23.9	23.6
C_2H_6	2.2	0.4	0.49	0.80
N_2	66.8	65.1	66.6	63.9
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.22	1.15	1.13	1.19
Condensate, gm. per 100 l. in-gas at N.T.P.				
CH_3OH	0.018	0.264	0.246	0.291
CH_2O	0.013	0.086	0.088	0.051
HCOOH	0·0	0·0	0·0	0·0
H_2O	9.04	8.99	9.10	11.42
Alcohol in condensate, %	0.198	2.84	2.60	2.48
Total carbon oxidized, %	13.0	22.1	22.1	25.6
Yields, as % of total carbon burned to:				
CH_3OH	0.348	3.01	2.76	2.84
CH_2O	0.275	1.04	1.05	0.53
HCOOH	0·0	0·0	0·0	0·0
Total	0.623	4.05	3.81	3.35
Total inlet oxygen accounted for, %	62.3	79.8	71.6	88.4

No. 49, vigorous reaction occurred and explosions took place. During the explosions, a copious deposit of soft carbon was formed on the catalyst; this deposit was caused probably by pyrolysis of methane and by the decomposition of oxidation products. While a material balance is given for No. 49, it is incorrect in not including the deposited carbon. The explosions were promoted by steel surfaces, and when reaction was confined to copper surfaces, they did not occur. Experiments 50, 51, and 52 are such experiments, and in no case was any carbon deposited in the apparatus. The yields are small and independent for all practical purposes of pressure and rate of flow.

Some information on the effect of pressure was given by these preliminary experiments. The effect of a 50 atm. increase was so small as to be almost negligible. Yields were lowered, and the amount of carbon burned increased slightly.

Effect of Oxygen Concentration

The effect upon the reactions of inlet oxygen concentration is illustrated by the data given in Table II and by Graphs I and II, Fig. 3. The yield of

TABLE II

EXPERIMENTS AT 350° C. AND 185 ATM. PRESSURE, SHOWING THE EFFECT OF OXYGEN
CONCENTRATION ON YIELD

Experiment No.	76	77	66	67	60	69	58	59
Off-gas flow, litres per min.	0.85	0.78	0.84	0.86	0.83	0.83	0.80	0.82
In-gas analysis								
O_2	3.47	3.76	6.15	8.45	10.8	10.33	12.0	13.2
CH_4	78.0	76.4	63.8	54.0	43.8	46.8	38.8	33.4
C_2H_6	1.02	1.88	2.11	1.79	1.45	1.21	1.21	1.1
N_2	17.51	17.96	27.94	35.76	43.95	41.66	47.99	52.3
Off-gas analysis								
CO_2	0.53	0.61	1.26	1.76	3.29	2.15	3.31	3.52
O_2	0.21	0.32	0.21	0.74	0.55	0.68	0.65	0.52
H_2	0.53	0.47	0.56	0.82	0.53	1.16	1.17	1.03
CO	1.30	1.21	1.98	2.57	1.22	3.23	2.11	1.97
CH_4	78.7	77.8	68.1	55.8	47.1	45.1	40.1	34.2
C_2H_6	0.65	1.1	0.38	0.31	0.51	0.12	0.1	0.63
N_2	18.08	18.49	27.5	38.0	46.8	47.56	52.6	58.13
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.04	1.04	1.1	1.08	1.15	1.07	1.14	1.17
Condensate, gm. per 100 l. in-gas at N.T.P.								
CH_3OH	1.74	1.73	2.16	2.06	1.46	1.84	1.37	0.96
CH_2O	0.195	0.198	0.202	0.159	0.137	0.126	0.114	0.101
HCOOH	0.034	0.031	0.049	0.063	0.015	0.061	0.016	0.011
H_2O	2.76	2.46	5.07	6.32	7.67	8.98	8.64	8.73
Alcohol in condensate, %	36.9	39.0	28.8	23.9	15.7	16.7	13.5	9.82
Total carbon oxidized, %	3.94	3.92	6.73	9.73	10.8	13.1	14.2	15.3
Yields, as % of total carbon burned to:								
CH_3OH	38.7	38.8	33.2	25.9	20.3	20.0	16.5	12.34
CH_2O	4.64	4.75	3.32	2.12	2.02	1.45	1.46	1.39
HCOOH	0.52	0.48	0.52	0.51	0.14	0.46	0.14	0.10
Total	43.86	44.03	37.04	28.54	22.46	21.91	18.1	13.73
Total inlet oxygen accounted for, %	107.0	99.0	101.4	95.0	85.0	101.2	86.3	81.5

useful products falls off linearly with an increase in oxygen concentration in the mixture. The slope of Graph I, giving total yield, is about −3.1, which may be considered a large rate of increase of yield with decreasing oxygen concentration. Graphs I and II show convergence at the higher

oxygen concentration; this shows that the proportion of formaldehyde and formic acid is nearly constant, lying between 10 and 11% of the total yield. The production of water and carbon oxides increases regularly with increasing oxygen concentration. As would be expected, the concentration of methanol in the condensate parallels the yield, and the relation to oxygen concentration is linear. Evidently, low oxygen concentrations are necessary for high yields of useful products, and also, for high concentrations in the condensate.
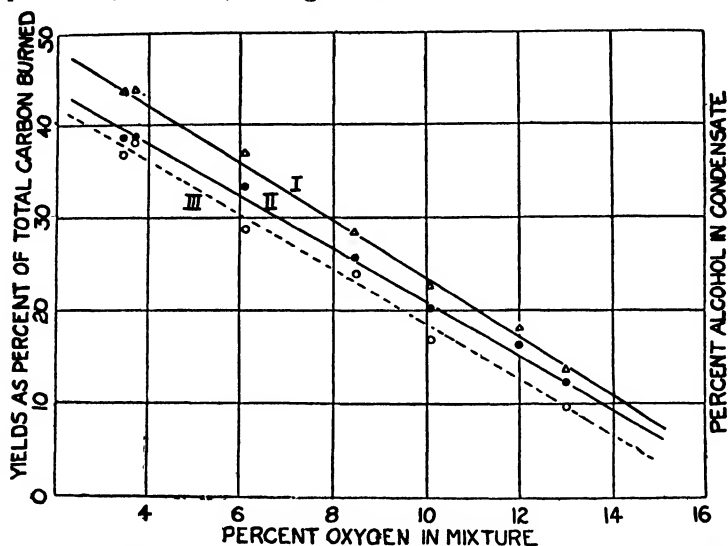
FIG. 3. *Yields as a function of oxygen concentration, from Table II. I, total useful oxygen compounds; II, methanol; III, weight per cent methanol in liquid condensate.*
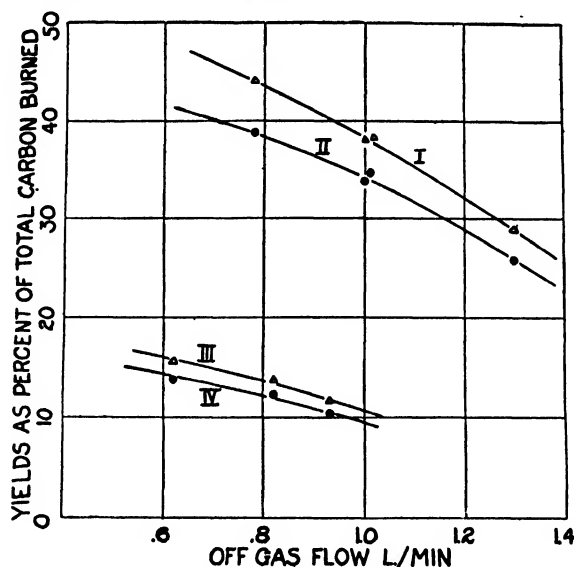
FIG. 4. *Yields as a function of off-gas flow, from Table III. I and II; total useful oxygen compounds and methanol respectively at a low oxygen concentration; III and IV, the same at a high oxygen concentration.*

The relation between the amount of carbon oxidized and the oxygen concentration can be seen by inspection of Table II. A linear relation is, of course, obtained. The results are of interest chiefly from the practical point of view when taken in conjunction with Graph I of Fig. 3. Obviously the greatest consumption of carbon per pass is desired in practice, with as great an efficiency of conversion to useful products as possible. The two requirements are in opposition, however; as carbon oxidized increases from 4 to 8%, the yield drops from 45 to 30% with increasing oxygen concentration. The greatest yield of useful products, 2.9%, occurs when the oxygen concentration is about 10%, but only 22% of the carbon oxidized enters into the formation of useful products.

TABLE III

EXPERIMENTS AT 350° C. AND PRESSURES NEAR 185 ATM., SHOWING THE EFFECT OF RATE OF FLOW ON YIELDS FOR TWO OXYGEN CONCENTRATIONS

Experiment No.	55	59	53	77	80	81	79
Pressure in atm.	188	182	168	185	188	185	188
Off-gas flow, litres per min.	0.62	0.82	0.93	0.78	1.0	1.04	1.30
In-gas analysis							
O_2	12.68	13.2	12.9	3.76	3.68	3.66	3.73
CH_4	35.56	33.4	34.9	76.4	75.3	75.4	75.3
C_2H_6	1.19	1.1	1.15	1.88	2.42	2.63	2.66
N_2	50.57	52.3	51.05	17.96	18.6	18.31	18.31
Off-gas analysis							
CO_2	3.6	3.52	3.0	0.61	1.07	0.95	2.45
O_2	0.7	0.52	0.3	0.32	0.21	0.21	0.5
H_2	0.8	1.03	2.7	0.47	0.42	0.53	0.5
CO	2.9	1.97	4.3	1.21	1.08	1.24	1.21
CH_4	36.4	34.2	33.8	77.8	78.5	77.6	75.0
C_2H_6	0.2	0.63	0.2	1.1	0.81	1.5	1.48
N_2	55.4	58.13	55.7	18.49	17.9	17.97	18.86
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.17	1.17	1.14	1.04	1.04	1.04	1.03
Condensate, gm. per 100 l. in-gas at N.T.P.							
CH_3OH	1.30	0.96	1.06	1.73	1.60	1.72	1.83
CH_2O	0.127	0.101	0.103	0.198	0.166	0.151	0.185
HCOOH	0.014	0.011	0.016	0.031	0.037	0.040	0.033
H_2O	9.79	8.73	9.88	2.46	2.76	2.35	2.11
Alcohol in condensate, %	11.6	9.82	9.58	39.0	35.1	40.3	44.0
Total carbon oxidized, %	17.3	15.3	19.5	3.92	4.16	4.31	6.17
Yields, as % of total carbon burned to:							
CH_3OH	13.9	12.34	10.3	38.8	33.8	34.6	25.8
CH_2O	1.44	1.39	1.06	4.75	3.72	3.25	2.77
HCOOH	0.11	0.1	0.1	0.48	0.54	0.57	0.32
Total	15.45	13.73	11.46	44.03	38.06	38.32	28.9
Total inlet oxygen accounted for, %	92.2	81.5	88.4	99.0	111.0	• 105.0	146.0

Effect of Rate of Flow

Some data illustrating the effect of rate of flow of the gas mixture over the catalyst are given in Table III and illustrated in Fig. 4. The change in yield with increasing rate of flow is in the same direction for both oxygen concentrations. Within the limits investigated, the yield falls off slowly with increasing rate of flow. This, of course, is only to be expected, and it might be predicted that at lower rates of flow than those used, a falling-off in yield would occur also. Thus, an optimum rate of flow resulting in maximum yield could be found somewhat lower than the lowest rate used. The other products of the experiments behave in a manner to be expected with changing yield of useful products.

Effect of Temperature

The effect of temperature at two different oxygen concentrations is shown by the data of Table IV. The data of Experiments 53, 56, and 57, in which 12.7% oxygen was used, show clearly a decrease in yield with increasing temperature, a 50% decrease for a 50° C. rise. Production of water increased, as did that of carbon monoxide and hydrogen in the off-gas. The apparent survival of ethane at the higher temperatures may not be real. The amounts are small and almost within experimental error, but the observation is emphasized because of its relation to other experiments.

The data of Experiments 85 to 93, in which a lower oxygen concentration was used, show no clearly marked trend with temperature. The yields are higher than those obtained in similar experiments the results of which are given in Table II (compare No. 77 with 93), and suggest an improvement in the catalyst with age. A poisoning action, which may be suspected in the experiments of Table II, will be discussed later.

It is interesting to notice the survival of ethane in all the experiments of Table IV at the lower oxygen concentration, and possibly an increase in ethane at the higher temperatures. This is contrary to what might be expected, since ethane is less stable than methane. The results of duplicate experiments were erratic, but there was no doubt as to the occurrence of hydrocarbons higher than methane. At 425° C. unknown gaseous compounds appeared in the off-gas. These compounds were hydrocarbons, insoluble in fuming sulphuric acid but oxidized by hot copper oxide. They interfered with the hydrogen and carbon monoxide determinations and consequently material balances could not be made. One experiment, No. 91, is included, and the yields are good.

Poisoning of the Catalyst

Some experiments illustrating loss of activity of the copper catalyst are given in Table V. Experiments 62, 63, and 64 may be compared with similar experiments the results of which are given in Table II, namely, Nos. 66, 67, and 76 or 77. Poisoning was very evident and could easily be detected, without going through all the analytical procedure, by the greater heat input to the reactor. It was due invariably to failure of the purification system, with

TABLE IV

EXPERIMENTS AT PRESSURES NEAR 185 ATM. AND RATES OF FLOW NEAR 1.0 LITRE PER MIN. SHOWING THE EFFECT OF TEMPERATURE ON YIELDS FOR TWO OXYGEN CONCENTRATIONS

Experiment No.	57	53	56	92	86	87	93	88	85	91
Temperature, °C.	325	350	375	325	325	325	350	350	400	425
Pressure in atm.	180	168	178	185	185	185	185	186	185	185
Off-gas flow, litres per min.	0.8	0.93	0.86	0.9	0.95	1.0	0.94	1.08	0.94	1.00
In-gas analysis										
O_2	12.7	12.9	12.5	3.98	4.1	3.89	4.22	3.63	3.71	3.68
CH_4	35.7	34.9	36.4	73.65	72.2	74.7	72.35	77.1	73.8	77.1
C_2H_6	1.2	1.15	1.2	2.73	2.76	2.14	3.20	2.61	2.03	2.0
N_2	50.4	51.05	49.9	19.64	20.94	19.27	20.23	17.24	19.88	17.2
Off-gas analysis										
CO_2	3.0	3.0	2.6	0.63	0.58	0.58	0.74	0.47	0.53	0.42
O_2	2.6	0.3	0.6	0.39	0.0	0.19	0.21	0.19	0.0	0.0
H_2	1.3	2.7	2.4	0.47	0.63	0.50	0.37	0.56	0.53	–
CO	2.5	4.3	5.5	0.14	0.63	0.72	0.21	0.63	0.53	–
CH_4	37.7	33.8	34.3	74.6	74.9	75.8	73.1	78.75	75.1	–
C_2H_6	0.0	0.2	0.3	2.53	1.81	2.01	3.45	1.79	2.68	–
N_2	52.9	55.7	54.3	21.24	21.45	20.2	21.92	17.61	20.63	–
Volume in-gas / Volume off-gas	1.16	1.14	1.09	1.03	1.03	1.02	1.05	1.05	1.05	1.00
Condensate, gm. per 100 l. in gas at N.T.P.										
CH_3OH	0.953	1.06	0.695	1.70	2.20	2.12	1.80	1.83	1.97	2.06
CH_2O	0.153	0.103	0.093	0.147	0.194	0.187	0.153	0.224	0.198	0.094
$HCOOH$	0.008	0.016	0.024	0.026	0.063	0 057	0 0	0.028	0.02	0.01
H_2O	8.78	9.88	12.66	2.53	2.90	2.70	2.70	2.12	2.66	3.15
Alcohol in condensate, %	9.62	9.58	5.16	38.6	41.0	41.9	38.7	43.4	40.6	38.8
Total carbon oxidized, %	14.7	19.5	20.6	2.6	3.73	3.72	2.90	3.10	3.24	–
Yields, as % of total carbon burned to:										
CH_3OH	12.0	10.3	6.1	58.0	53.3	51.0	55.5	51.0	54.3	–
CH_2O	2 04	1.06	0.86	5.53	5.02	4.77	5.0	6.65	5.75	–
$HCOOH$	0.143	0.1	0.14	0 62	1.06	0.95	0.0	0.54	0.37	–
Total	14.2	11.46	7.10	64 15	59.38	56.72	60.5	58.19	60.42	–
Total inlet oxygen accounted for, %	93.0	88.4	107.0	78.5	87.0	88.6	81.0	83.0	87.0	–

consequent introduction of sulphur or the admission of heavy oils and vapors. Generally, the system was cleaned thoroughly and the catalyst washed with dilute nitric acid to clear up the trouble. Mere traces of poisons difficult to detect, other than by means of the effect on the catalyst, were sufficient to reduce catalytic activity.

The remaining experiments in Table V illustrate the abrupt poisoning of the catalyst and its slow regeneration. This was shown by letting the reactions take place over a long period of time. The period was divided into three experiments, Nos. 73, 74, and 75. The catalyst was poisoned by sulphur in

TABLE V

EXPERIMENTS AT 350° AND 185° C., SHOWING THE EFFECTS OF POISONING THE
CATALYST AT TWO OXYGEN CONCENTRATIONS

Experiment No.	72	73	74	75	62	63	64
Off-gas flow, litres per min.	0.87	0.68	0.79	0.71	0.76	0.77	0.98
In-gas analysis							
O_2	3.95	3.82	3.80	3.69	6.81	8.62	3.53
CH_4	74.8	74.7	75.5	75.7	61.0	53.3	76.7
C_3H_6	2.05	2.24	2.0	1.93	2.02	1.76.	1.93
N_2	19.2	19.24	18.62	18.68	30.17	36.33	17.6
Off-gas analysis							
CO_2	1.92	1.40	0.84	0.74	1.86	2.16	1.16
O_2	0.34	0.32	0.38	0.53	0.52	0.84	0.42
H_2	0.42	0.35	0.42	0.37	0.31	0.63	0.21
CO	0.85	0.84	1.35	1.27	1.67	'2.27	0.79
CH_4	76.7	77.6	77.7	76.7	66.0	53.8	79.5
$C.H_6$	1.40	1.39	0.97	1.1	0.80	0.70	0.54
N_2	18.37	18.10	18.34	19.29	28.8	39.6	18.2
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.06	1.06	1.05	1.03	1.11	1.07	1.03
Condensate, gm. per l. in-gas at N.T.P.							
$CH.OH$	1.09	1.30	1.68	1.64	1.29	1.13	0.654
CH_2O	0.144	0.156	0.18	0.175	0.201	0.173	0.145
HCOOH	0.019	0.023	0.032	0.033	0.035	0.034	0.026
H_2O	2.58	2.40	2.31	2.21	6.64	7.95	3.25
Alcohol in condensate, %	28.6	33.5	40.0	40.3	15.8	12.1	16.0
Total carbon oxidized, %	4.45	4.0	4.3	4.07	6.52	8.96	3.07
Yields, as % of total carbon burned to:							
CH_3OH	22.0	29.0	34.5	35.6	21.4	15.5	18.6
CH_2O	3.06	3.7	3.94	4.03	3.55	2.55	4.4
HCOOH	0.26	0.35	0.45	0.5	0.32	0.40	0.51
Total	25.32	33.05	39.0	40.13	25.35	18.37	23.54
Total oxygen accounted for, %	116.0	106.0	102.7	105.0	98.2	108	120

Experiment 72, and the purification system was overhauled immediately. With continued use, an improvement in the activity of the catalyst took place. The rate of improvement fell off greatly, however, and normal activity, as in No. 77, Table II, was obtained only after the reaction system and catalyst had been cleaned.

The sensitivity of copper to poisons is a serious disadvantage from the practical point of view. Most natural gases contain sulphur, and its complete removal is difficult. A less sensitive catalyst or a method of operation that eliminates poisoning is highly desirable, and some attention has been given the matter in later work.

Conclusions

It may be concluded that the yield of useful products depends primarily on the catalyst, the oxygen concentration, and the temperature.   The influence of the time of reaction and the pressure, within the limits studied, is small. The catalyst chosen, copper, fulfils at least two functions in providing a metallic surface easily oxidized and reduced, and in aiding in the dissipation of the heat of reaction.   Gas phase reactions and lack of temperature control are both detrimental.   This suggests that the desired reactions take place on surfaces and are highly sensitive.

The general features of the results may be explained reasonably well on the basis of the "hydroxylation theory" (1).   Obvious confirmation of the theory lies in the production of large amounts of methanol and small amounts of formaldehyde and formic acid when the oxidation of methane is carried out under pressure.   The dependence of yield on oxygen concentration, or, in another way, the requirement of a large oxygen deficiency for high conversion to methanol, is also explicable on the basis of the theory.   Finally, many tests on the liquid and gaseous products of the reactions for peroxides were negative.

A great many details remain, however, unexplained.   Reference is to the minor products and the kinetics of the reactions.   It is believed that the chain mechanism advanced by Norrish (4) offers some help in this connection. Further experimental data are necessary, however, and will be presented together with a discussion in a later report.

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THE OXIDATION OF METHANE AT HIGH PRESSURES

III. EXPERIMENTS USING PURE METHANE AND PRINCIPALLY COPPER AS CATALYST[1]

By E. H. Boomer[2] and V. Thomas[3]

Abstract

Mixtures of methane containing some nitrogen and oxygen were passed over copper and silver catalysts. The effects of the variables, composition of mixture, pressure, and temperature were determined. From 3 to 7% of oxygen was used in various experiments at pressures from 140 to 220 atm. at a temperature of 475° C. The effect on yields of additions of carbon dioxide to the mixture was determined.

Introduction

Previous reports have described preliminary experiments (2) and a systematic investigation (4) on the oxidation by air of a natural gas of high methane content. The present report deals with experiments on methane, in which principally copper was used as catalyst, but including some work with other catalysts.

In earlier work, the presence of ethane and higher hydrocarbons in the natural gas used resulted in some ambiguity with regard to the results. It was impossible to decide just how much of the products of the reaction was due to methane and how much due to other hydrocarbons. In order to obtain a definite knowledge of the reactions taking place, the present series of experiments were carried out using a gas mixture, containing only methane, oxygen, and nitrogen. In the systematic investigations on the effect of variables such as pressure, temperature, composition, and rate of flow of gas, copper was used as catalyst. In addition some experiments were carried out with other catalysts.

Experimental

The experimental methods differed in some details from those described in previous reports. The difference was principally in the preparation of gas mixtures and control of pressures in the apparatus.

Materials

Natural gas from the Viking field near Edmonton was used as a source of methane. The higher hydrocarbons were removed by a method of pyrolysis followed by elimination of the products of pyrolysis which has been described (3). The gas had the composition by volume: methane, 94.3; nitrogen, 5.7%. Air was used as oxidant after drying over calcium chloride and removal of carbon dioxide with solid potassium hydroxide.

The catalysts used were copper, silver, a high nickel-chromium steel (Enduro KA2S), and glass. The copper catalyst was cut into $\frac{3}{16}$ in. squares, $\frac{3}{32}$ in. thick. It weighed 39.8 gm. and its volume was 4.46 cc. The silver catalyst was in the form of $\frac{3}{16}$ in. squares cut from 0.004 in. sheet. It weighed 15.35 gm. and its volume was 1.46 cc. The steel catalyst, in the form of machine turnings about 6 mesh in size, weighed 17.13 gm. and had a volume of 2.20 cc. The glass catalyst consisted of $\frac{3}{8}$ in. lengths of $\frac{1}{8}$ in. soft glass tubing. It weighed 8.16 gm. All catalysts occupied about the same space; namely, 12 cc. when packed in the reactor.

Apparatus

In these experiments the supply of methane was limited and only a small storage cylinder was used. In order to prevent a large pressure drop during the reaction, a storage and pressure control system as shown in Fig. 1. was
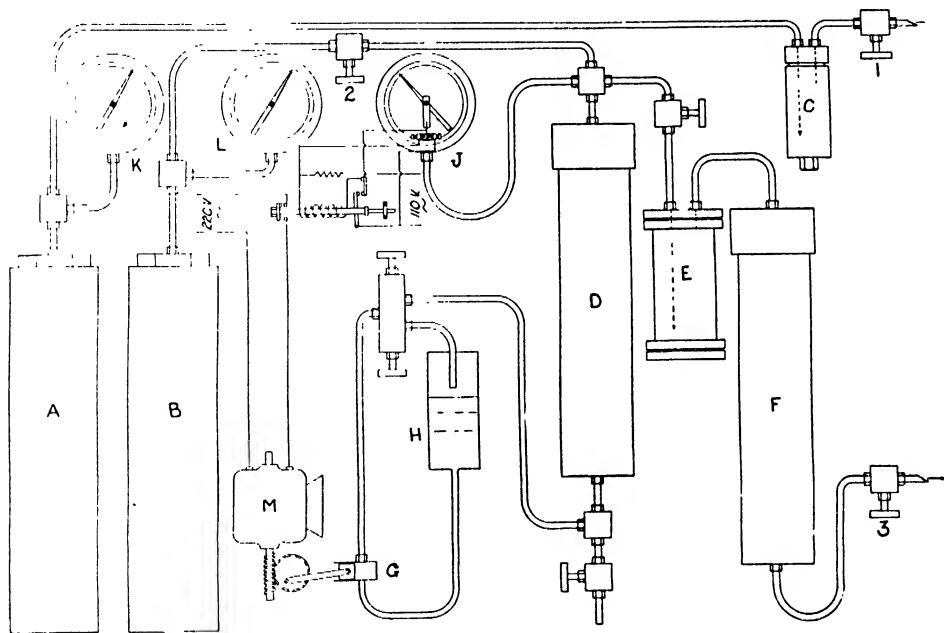
FIG. 1.   *Apparatus for automatic control of high gas pressures.*

devised. Large cylinders, *A* and *B*, contained air and methane respectively. The air storage pressure was some 35 atm. greater than the pressure to be used in an experiment, and the cylinder was of such size that the pressure dropped only a few atmospheres during the course of an experiment. Methane was taken from cylinder *B* to the hydraulic cylinder, *D*, and subsidiary storage cylinder, *F*. A hydraulic pump, *G*, was used to pump a 50% glycerine-water mixture into cylinder *D* until the pressure was equal to the experimental value required. Two contacts, high and low, on the pressure gauge, *J*, operating through a relay (G.E., 2904 G2) controlled the motor, *M*. As gas

was withdrawn through valve 3 to the reaction system, the movement of the gauge index operated the motor, and this resulted in entry of fluid to cylinder *D*, and a constant pressure. The system was sensitive to a pressure drop of less than one atmosphere, hardly discernible on the gauge.

The pressure bottle *C* contained solid potassium hydroxide, and valve 1 was connected through a check valve to the air control valve on the reaction system. The pressure bottle *E* contained, in order, calcium chloride and activated coconut charcoal to give the methane a final purification. Valve 3 was connected through a check valve to the gas control valve on the reaction system.

The reaction system and its operation has been described in detail (4), and does not require discussion except in one regard—the operating procedure is different. In the present case, the gas valve was opened and the system brought to the operating pressure as maintained by the control described above. The air valve was then opened and adjusted until the composition of the gas-air mixture was that desired as shown by the thermal conductivity analyses.

The analytical procedure followed with regard to the gas mixtures and products of the reaction, as well as occasional confirmations by ultimate analysis, was the same as that described previously (4). All analyses were made in duplicate and any doubtful results resulted in rejection of the experiment unless checks could be obtained.

Experimental Results

The results are presented in the form of tables giving the essential data and graphs illustrating salient features of the data. In all cases, the element carbon has been taken as the reference substance, and calculations of material balances have been made upon that basis. No evidence was ever obtained that carbon was lost in the apparatus or in the products in appreciable amounts, and, furthermore, the nitrogen balance was in general agreement with the carbon balance. The hydrogen balance showed greater and erratic errors but of no great significance. However, the oxygen balance, on the assumption that the carbon balance was correct, was greatly in error. There was invariably a loss of oxygen which was, except rarely, greater than any conceivable error of analysis, and it has not yet been possible to explain the loss in any reasonable manner. The same result was obtained previously (4), although not so consistently, and has been noticed elsewhere (6).

A result of some importance and interest was found immediately these experiments were begun. Temperatures of at least 350° C. were necessary to initiate oxidation of methane, and temperatures higher than 400° C. were the most satisfactory. The range 425° to 475° C. was found to produce the highest yields and was, as a consequence, generally used. The much lower temperatures (4) required with Viking natural gas may be attributed to the ethane and propane present. These gases would oxidize at a lower temperature than would methane, and possibly stimulate the oxidation of the more resistant methane.

Effect of Oxygen Concentration on Yields

Experiments showing the effect of oxygen concentration in the gas mixture on the yields of useful products at three different pressures are given in Tables I, II, and III. Figs. 2 and 3 illustrate graphically these results.   The reactions were very similar in behavior at all pressures, showing a rapid decrease in yield with increasing oxygen concentration.   The graphs of Fig. 2 are curved and show a rapid increase in slope at high oxygen concentrations, a result that may be compared with the straight lines obtained when Viking natural gas (4) is used in place of methane.   Another comparison is given in Fig. 3.   Here, the straight lines I and II have been taken from the data on natural gas.   The graphs for methane show a curvature and a maximum in the region of 6% oxygen.   It is of interest to note that this point of maximum consumption of carbon corresponds to the oxygen concentration at which the yields begin to fall off rapidly.

TABLE I

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C.
AND 141 ATM. PRESSURE

Experiment No.	154	153	155	156
Off-gas flow, litres/min.	0.89	0.90	0.89	0.84
In-gas analysis:				
O_2	2.77	4.42	6.32	8.35
CH_4	81.6	74.3	65.7	56.6
N_2	15.63	21.28	27.98	35.05
Off-gas analysis:				
CO_2	0.53	0.79	1.05	1.23
O_2	0.0	0.13	0.11	0.0
H_2	0.55	0.63	1.29	0.63
CO	0.0	0.0	0.24	0.0
CH_4	84.15	76.8	68.6	59.1
N_2	14.77	21.65	28.71	39.04
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.04	1.09	1.08
Condensate, gm./100 litres in-gas at N.T.P.				
Total	2.69	4.29	6.32	8.43
CH_3OH	1.01	1.30	1.35	0.778
CH_2O	0.0657	0.075	0.10	0.0973
HCOOH	0.0246	0.0409	0.0423	0.0477
H_2O	1.59	2.87	4.83	7.51
Alcohol in condensate, %	37.6	30.3	21.3	9.22
Total carbon oxidized, %	1.57	2.43	3.40	3.16
Yields, as % of total carbon burned to:				
CH_3OH	55.7	54.0	42.2	30.6
CH_2O	3.80	3.12	3.36	4.07
HCOOH	0.94	1.12	0.93	1.26
Total	60.44	58.24	46.49	35.93
Total inlet oxygen accounted for, %	68.0	71.8	74.5	80.5

A similar, though not pronounced, difference exists with regard to the concentration of alcohol in the condensate. Instead of showing a linear relation a curve is obtained showing a greater slope at higher oxygen concentrations.

No definite conclusions can be drawn with regard to the minor constituents of the off-gases. Possibly the observation of most interest was the absence of carbon monoxide in the products obtained at lower oxygen concentrations. This was generally true in all experiments with methane. It is significant of the effect of higher hydrocarbons that, in all experiments with natural gas, carbon monoxide was a product. Another significant feature that was observed was the formation of traces of higher hydrocarbons in all experiments with methane. The amounts were small and within the experimental error; they have not been listed. However, they were found consistently and it appeared that the amounts were greater at higher oxygen concentrations. The occurrence, to be discussed later, of traces of oils among the liquid products may be related to the above observation.

TABLE II

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C.
AND 184 ATM. PRESSURE

Experiment No.	115	99	116	117	118	119	137
Off-gas flow, litres/min.	0.84	0.80	0 81	0.77	0.83	0.79	0.78
In-gas analysis:							
O_2	3.22	4.85	5.53	6.93	7.0	7.9	8.63
CH_4	80.0	72.5	69.1	63.0	62.7	56.9	55.4
N_2	16.78	22.65	25.37	30.07	30.3	35.2	35.97
Off-gas analysis:							
CO_2	0.34	0.58	0.63	0.87	0.95	0.97	1.37
O_2	0.16	0.47	0.32	0.32	0.13	0.24	0.13
H_2	0.26	0.26	0.37	0.45	0.05	0.58	1.84
CO	0.0	0.0	0.0	0.0	0.0	0.11	0.21
CH_4	81.4	74.9	72 9	66.4	66.6	61.5	58.6
N_2	17.84	23.79	25.78	31.96	32.27	36.6	37.85
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.04	1.04	1.09	1.08	1.09	1.11	1.10
Condensate, gm./100 litres in-gas at N.T.P.							
Total	3.78	5.05	5.44	6.27	6.43	4.88	8.05
CH_3OH	1.60	1.66	1.57	1.15	1.27	0.69	0.621
CH_2O	0.078	0.051	0.077	0.07	0.081	0.079	0.076
HCOOH	0.0304	0.0441	0.0314	0.0306	0.0324	0.0249	0.0244
H_2O	2.07	3.30	3.75	5.02	5.05	4.09	7.33
Alcohol in condensate, %	42.2	32.9	29.0	18.5	19.7	14.1	7.72
Total carbon oxidized, %	1.90	2.48	2.54	2.66	2.90	2.70	3.52
Yields, as % of total carbon burned to:							
CH_3OH	74.0	65.3	62.8	48.2	49.2	31.6	22.4
CH_2O	3.82	2.16	3.28	3.12	2.16	3.84	2.94
HCOOH	0.98	1.20	0.87	0.91	0.86	0.90	0.62
Total	78.8	68.66	66.95	52.23	52.22	36.34	25.96
Total inlet oxygen accounted for, %	73.6	76.3	69.0	67.6	66.4	50.4	73.0

The Effect of Pressure on Yields

The effect of pressure may be seen from a study of Tables I, II, and III and Fig. 2. Over most of the range of oxygen concentrations, the yield passed through a maximum as the pressure was raised from 141 to 231 atm. The yield at 184 atm. was greater than that at the lower and higher pressures. However, at a concentration of 7% of oxygen the graphs begin to cross, and ultimately the highest yield is obtained at a pressure of 141 atm. At these high oxygen concentrations the yields were very low and the experiments difficult to control. Little weight can be placed on the results, and it might be said that pressure had little or no effect at high oxygen concentrations. However, there was no doubt as to the reality of the effect at low oxygen concentrations, an effect explicable only when the kinetics of the reactions is known.

TABLE III

EXPERIMENTS WITH DIFFERENT OXYGEN CONCENTRATIONS CARRIED OUT AT 475° C.
AND 231 ATM. PRESSURE

Experiment No.	151	146	144	143
Off-gas flow, litres/min.	0.84	0.84	0.84	0.84
In-gas analysis:				
O_2	3.18	4.42	6.73	8.74
CH_4	79.8	74.3	63.9	54.9
N_2	17.02	21.28	29.37	36.36
Off-gas analysis:				
CO_2	0.53	0.63	1.05	1.26
O_2	0.0	0.05	0.16	0.13
H_2	0.5	0.55	1.55	2.03
CO	0.0	0.0	0.11	0.34
CH_4	82.5	77.5	67.2	38.0
N_2	16.47	21.27	29.93	38.24
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.06	1.09	1.09
Condensate, gm./100 litres in-gas at N.T.P.				
Total	3.26	4.81	6.61	8.20
CH_3OH	1.34	1.67	1.54	0.694
CH_2O	0.0604	0.0833	0.0965	0.0633
$HCOOH$	0.0195	0.0447	0.0435	0.0523
H_2O	1.84	3.02	4.93	7.40
Alcohol in condensate, %	41.0	34.9	23.3	8.46
Total carbon oxidized, %	1.87	2.49	3.48	3.67
Yields, as % of total carbon burned to:				
CH_3OH	62.7	63.2	48.6	24.2
CH_2O	3.03	3.36	3.24	2.30
$HCOOH$	0.63	1.18	0.95	1.25
Total	66.36	67.74	52.8	27.75
Total inlet oxygen accounted for, %	67.7	72.2	73.0	72.5
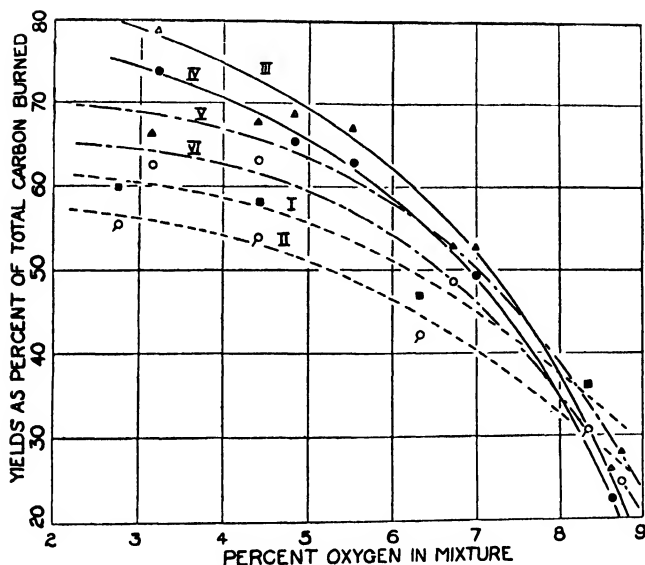
FIG. 2.   Yields as a function of oxygen concentration and pressure, from Tables I, II, and III.   I, III, and V; total useful oxygen compounds at 141, 184, and 231 atm. respectively: II, IV, and VI; methanol at the same pressures.
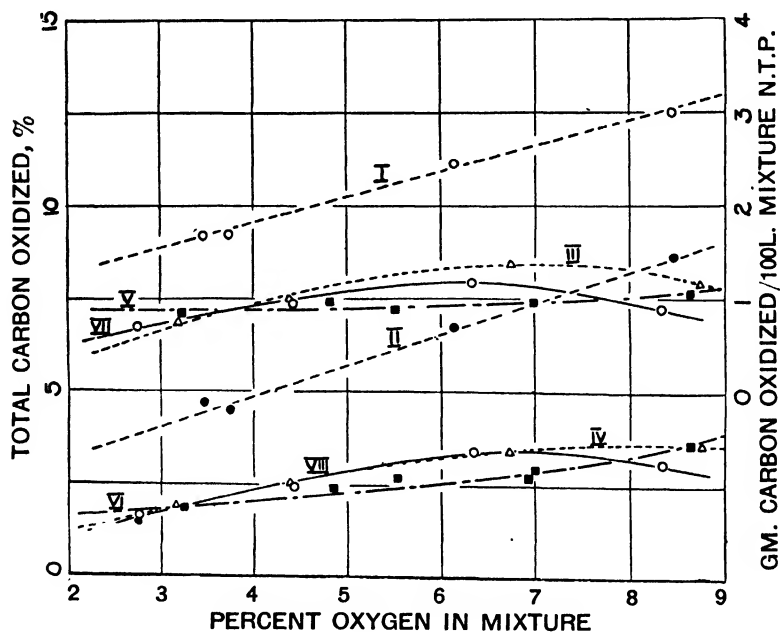
FIG. 3.   Carbon oxidized as a function of oxygen concentration and pressure, from Tables I, II, and III.   Even numbered curves, per cent, odd numbered curves, grams.   I and II, natural gas; III and IV, V and VI, VII and VIII, for 141, 184, and 231 atm. pressure respectively.

Effect of Temperature on Yields

A considerable number of experiments were carried out under various conditions to determine the effect of different temperatures on yields.   The results are given in Tables IV, V, VI, and VII, and illustrated in Figs. 4 and 5.   The data of Tables V and VII are shown in Fig. 4, and give the results for two pressures at low oxygen concentrations.   Obviously there is an optimum temperature around 450° C. which is the same for both pressures.   It was interesting to note during these experiments that control of the reactions was much easier at temperatures higher than 400° C. than below.

TABLE IV

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 231 ATM. PRESSURE,
USING ABOUT 8.7% OF OXYGEN

Experiment No.	140	139	138	142	143
Temperature, °C.	360	390	390	425	475
Off-gas flow, litres/min.	0.79	0.80	0.93	0.80	0.84
In-gas analysis:					
O_2	8.74	8.54	8 30	8 74	8.74
CH_4	54.9	55.8	56.7	54.9	54.9
N_2	36.36	35.66	35.0	36.36	36 36
Off-gas analysis:					
CO_2	2.28	2 08	2.16	1.68	1 26
O_2	0.47	0.16	0.13	0.26	0.13
H_2	0.47	0.63	0.61	1.34	2.03
CO	0.0	0.16	0.10	0.20	0 34
CH_4	58.7	58.7	59.35	58.4	58.0
N_2	38.08	38.27	37.65	38.03	38.24
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.14	1.12	1.11	1.12	1.09
Condensate, gm./100 litres in-gas at N.T P.					
Total	8.55	8.69	8.44	8.39	8.20
CH_3OH	1.74	1.91	1.85	1.37	0 694
CH_2O	0.116	0.114	0.104	0.0908	0.0633
HCOOH	0.0707	0 0407	0.0411	0.0596	0 0523
H_2O	6.63	6.63	6.43	6.87	7.40
Alcohol in condensate, %	20.4	22.0	21.9	16.4	8.46
Total carbon oxidized, %	6.13	6.18	6.05	5 13	3.67
Yields, as % of total carbon burned to:					
CH_3OH	37.0	38.8	37.8	34.2	24.2
CH_2O	2.58	2.48	2.26	2.42	2.30
HCOOH	1.03	0.58	0.59	1 03	1.25
Total	41.61	41.86	40.65	37.65	27.75
Total inlet oxygen accounted for, %	82.8	81.0	82.2	76.5	72.5

The stability of the copper catalyst as regards temperature was demonstrated by these experiments. Between Experiments 94 and 101, Table VII, the temperature was varied from 350° to 500° C. without any intermediate activations, and yet the two experiments agreed well with each other.

The data of Tables IV and VI, shown graphically in Fig. 5, give the effect of temperature at two pressures and high oxygen concentrations. The optimum temperature was lowered to 390°C. by increasing the oxygen concentration, but it was still nearly independent of pressure.

TABLE V

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 231 ATM. PRESSURE, USING ABOUT 4.4% OF OXYGEN

Experiment No.	149	150	147	145	146	148
Temperature, °C.	390	425	425	475	475	506
Off-gas flow, litres/min.	0.90	0.84	0.88	0.86	0.84	0.87
In-gas analysis:						
O_2	4.28	4 48	4.42	4 42	4.42	4.42
CH_4	74.8	73.8	74.3	74.3	74.3	74.3
N_2	20.92	21.72	21.28	21.28	21.28	21.28
Off-gas analysis:						
CO_2	0.84	0.79	0.83	0.73	0.63	0 73
O_2	0.0	0.11	0.0	0.13	0.05	0.05
H_2	0.37	0.50	0.53	0.89	0.55	0.82
CO	0.0	0.0	0.0	0.0	0.0	0.0
CH_4	77.8	77.8	77.4	77.2	77.5	77.1
N_2	20.99	20.8	21.24	21.02	21.27	21.3
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.06	1.08	1.06	1.07	1.06	1.06
Condensate, gm./100 litres in-gas at N.T.P.						
Total	4.84	4.73	4.79	4.70	4.81	4.48
CH_3OH	1.74	1.72	1.63	1.66	1.67	1.42
CH_2O	0.109	0.081	0.078	0.0743	0.0833	0.0769
HCOOH	0.0273	0.026	0.0412	0.0454	0.0447	0.0361
H_2O	2.96	2.90	3.04	2.92	3.02	2.94
Alcohol in condensate, %	35.8	36.4	34.0	35.3	34.9	31.8
Total carbon oxidized, %	2.81	2.75	2.70	2.61	2.49	2.39
Yields, as % of total carbon burned to:						
CH_3OH	58.0	60.2	57.2	60.4	63.2	56.3
CH_2O	3.85	3.02	2.91	3.16	3.36	3.24
HCOOH	0.62	0.63	0.99	1.15	1.18	0.99
Total	62.47	63.85	61.10	64.71	67.64	60.53
Total inlet oxygen accounted for, %	77.8	73.2	73.3	74.5	72.2	73.0

The weight and composition of the liquid condensate did not vary greatly with temperature, the variation in yield being accounted for by variations in the amount of carbon oxidized. However, at the higher oxygen concentrations, the alcohol content paralleled the yield roughly. The changes in the composition of the off-gas were hardly significant except in one regard. As has been noted before, no carbon monoxide was found at any temperature with low oxygen concentrations, but was always present at high oxygen concentrations.

TABLE VI

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 184 ATM. PRESSURE,
USING ABOUT 8.7% OF OXYGEN

Experiment No.	126	135	130	133	132	136	137
Temperature, °C.	350	375	390	390	390	425	475
Off-gas flow, litres/min.	0.84	0.81	0.82	0.85	0.85	0.78	0.78
In-gas analysis:							
O_2	8.64	8.60	8.71	8.68	8.54	8.74	8 63
CH_4	55.4	55.5	55.0	55.2	55.8	54.9	55.4
N_2	35.96	35 9	36.29	36.12	35.66	36 36	35.97
Off-gas analysis:							
CO_2	2.00	2 42	2.09	2.52	2 52	1.79	1.37
O_2	0.11	0 11	0.05	—	0 11	0.21	0.13
H_2	1.16	0.58	0.82	0.61	0.71	1.16	1.84
CO	0 63	0.11	0.18	0.11	0.11	0.21	0.21
CH_4	58.55	57.9	59.1	58.3	58.1	58 0	58.6
N_2	37.55	38.88	37.76	38.46	38.45	38.63	37.85
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.10	1.11	1.11	1.13	1.11	1 11	1.10
Condensate, gm./100 litres in-gas at N.T.P.							
Total	8 53	8.27	8.75	8.34	8.35	8 39	8.05
CH_3OH	1.54	1.59	1.76	1.63	1.61	1 08	0.621
CH_2O	0.125	0.113	0.118	0.111	0.113	0.112	0.763
HCOOH	0.0388	0.0367	0.0432	0.0219	0.0306	0.0286	0.0244
H_2O	6.83	6.53	6.83	6.58	6.60	7 17	7 33
Alcohol in condensate, %	18.1	19.2	20.2	19.5	19.3	12.8	7.72
Total carbon oxidized, %	6.49	6.25	6.15	6.42	6.41	4.84	3.52
Yields, as % of total carbon burned to:							
CH_3OH	30.2	31.4	36.8	32.2	31.7	28.5	22.4
CH_2O	2.60	2.41	2.60	1.54	1.54	3.16	2.94
HCOOH	0.53	0.49	0.62	0.30	0.40	0.54	0.62
Total	33.3	34.3	40.02	34.04	33.64	32.2	25.96
Total inlet oxygen accounted for, %	81.7	81.6	80.0	81.0	83.7	79.2	73.0

TABLE VII

EXPERIMENTS AT DIFFERENT TEMPERATURES AND 184 ATM. PRESSURE,
USING ABOUT 4.9% OF OXYGEN

Experiment No.	94	95	96	97	98	99	100	101
Temperature, °C.	350	375	400	425	450	475	500	350
Off-gas flow, litres/min.	0.73	0.70	0.78	0.66	0.79	0.80	0.74	0.74
In-ga analysis:								
O_2	4.86	4.96	5.03	4.85	4.85	4.85	4.85	4.85
CH_4	72.9	72.0	72.6	73.0	73.0	72.5	72.5	72.5
N_2	22.24	23.04	22.36	22.15	22.15	22.65	22.65	22.65
Off-gas analysis:								
CO_2	0.95	0.95	0.74	0.65	0.63	0.58	0.63	0.97
O_2	0.26	0.21	0.53	0.24	0.16	0.47	0.26	0.26
H_2	0.24	0.19	0.16	0.23	0.21	0.26	0.21	0.16
CO								
CH_4	75.45	74.8	74.2	75.4	75.5	74.9	75.2	75.3
N_2	23.1	23.85	24.37	23.48	23.39	23.79	23.7	23.31
$\dfrac{\text{Volume in-gas}}{\text{Volume off gas}}$	1.05	1.07	1.05	1.04	1.04	1.04	1.04	1.05
Condensate, gm./100 litres in-gas at N.T.P.								
Total	5.00	4.78	5.17	5.38	5 25	5.05	4.75	5.26
CH OH	1.67	1.57	1.73	1.82	1.76	1.66	1.40	1.74
CH_2O	0.134	0.115	0.158	0.139	0.0586	0 0508	0.0474	0.148
HCOOH	0.084	0.0726	0.0604	0.0814	0 0441	0.0441	0.0305	0.0505
H_2O	3.12	3.02	3.22	3.34	3.39	3.30	3.27	3.32
Alcohol in condensate, %	33.3	32.9	33.4	33.9	33.6	32.9	29.6	33.1
Total carbon oxidized, %	3.03	2.93	2.85	2.80	2.61	2.48	2.26	3.14
Yields, as % of total carbon burned to:								
CH_3OH	52.7	52.2	58.8	62.5	65.1	65.3	60.2	53.4
CH_2O	4.53	4.08	5.07	5.07	2.26	2.16	2.16	4.85
HCOOH	1.85	1.67	1.42	1.94	1.12	1.20	0.93	1.08
Total	59.08	57.95	65.92	69.51	68.48	68.66	63.29	59,33
Total inlet oxygen accounted for, %	79.0	72.6	77.7	75.3	72.8	76.3	70.2	81.2
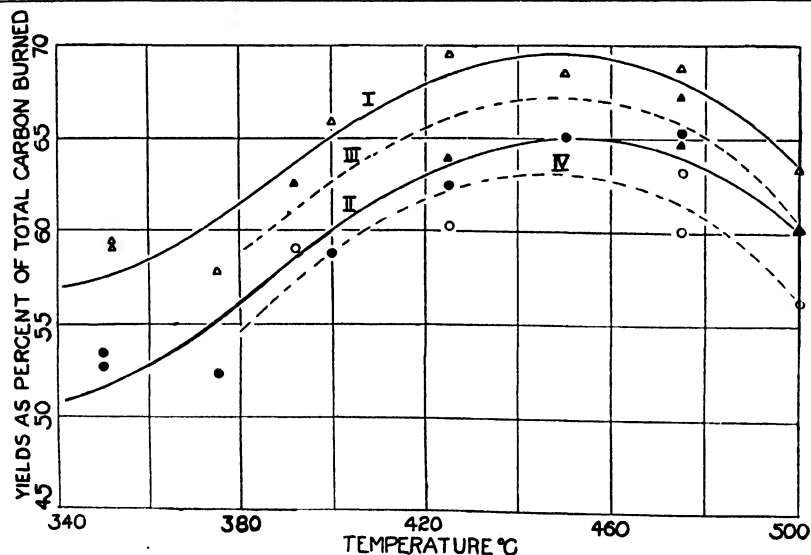
FIG 4.   *Yields as a function of temperature, from Tables V and VII.   I and II, total useful oxygen compounds and methanol respectively at 184 atm.; III and IV, the same at 231 atm.*
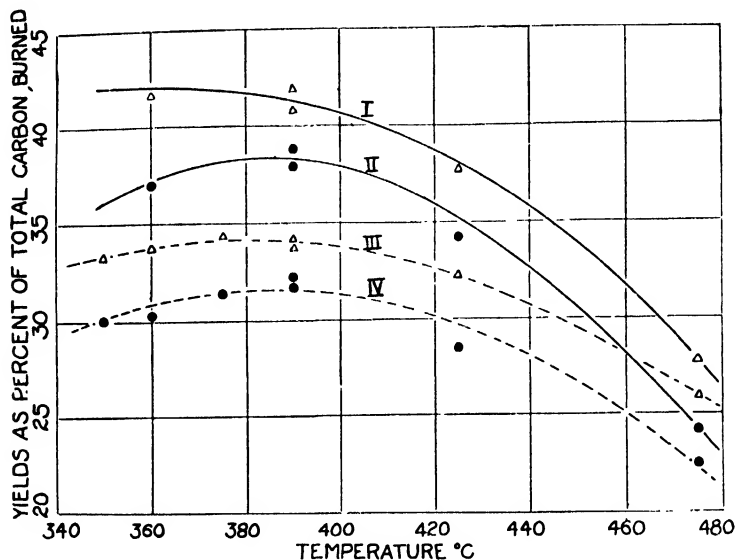
FIG. 5. *Yields as a function of temperature from Tables IV and VI. I and II, total useful oxygen compounds and methanol respectively at 184 atm.; III and IV, the same at 231 atm.*

TABLE VIII

EXPERIMENTS AT DIFFERENT RATES OF GAS FLOW AND 184 ATM. PRESSURE, USING
ABOUT 4.9 AND 8.7% OF OXYGEN AT 475° AND 360° C. RESPECTIVELY

Experiment No.	108	99	110	111	125	134	127
Temperature, °C.	475	475	475	475	360	360	360
Off-gas flow, litres/min.	0.66	0.80	0.89	1.03	0.62	0.79	0.99
In-gas analysis:							
O_2	4.85	4.85	4.87	4.95	8.64	8.70	8.64
CH_4	72.7	72.5	72.7	72.3	55.4	55.0	55.4
N_2	22.45	22.65	22 43	22.75	35.96	36.3	35.96
Off-gas analysis:							
CO_2	0.63	0.58	0.53	0.63	2.16	2.52	1.92
O_2	0.31	0.47	0.21	0.16	0.32	0.11	0.16
H·	0.11	0.26	0.26	0.11	0.71	0.68	1.16
CO	0.0	0.0	0.0	0.0	0.63	0.11	0.42
CH_4	75.0	74.9	75.5	75.2	58 1	58.1	59.5
N_2	23.95	23.79	23.5	23.8	38.08	38.48	36.84
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.05	1.04	1.05	1.06	1.10	1.13	1.11
Condensate, gm./100 litres in-gas at N.T.P.							
Total	5.06	5.05	5.25	5.28	8.71	7.95	8.48
CH_3OH	1.64	1.66	1.70	1.69	1.75	1.48	1.58
CH_2O	0.0472	0.0508	0.0607	0.0698	0.150	0.130	0.121
HCOOH	0.0404	0.0441	0.0337	0.0299	0.0479	0.0392	0.0463
H_2O	3.33	3.30	3.46	3.49	6.76	6.30	6.73
Alcohol in condensate, %	32.4	32.9	32.4	32.1	20.1	18.6	18.6
Total carbon oxidized, %	2.48	2.48	2.42	2.56	7.06	6.27	6.00
Yields, as % of total carbon burned to:							
CH_3OH	63.8	65.3	67.8	64.4	31.0	30.3	33.4
CH_2O	1.95	2.16	2.57	2.82	2 86	2.81	2.72
HCOOH	1.09	1.20	0.96	0.79	0.60	0.56	0.68
Total	66.84	68.66	71.33	68.01	35.06	33.67	36.8
Total inlet oxygen accounted for, %	74.0	76.3	72.0	72.0	86.3	79.5	79.6

Effect of Rate of Gas Flow on Yields

Table VIII and Fig. 6 show results illustrating changes in yield with rate of gas flow over the catalyst for two oxygen concentrations. The data are not particularly significant, especially at the higher oxygen concentration. A maximum appears in the graphs for low oxygen concentration and a minimum in the other case. A maximum might be expected, and would be observed more clearly no doubt if a wider range of gas flows had been used.
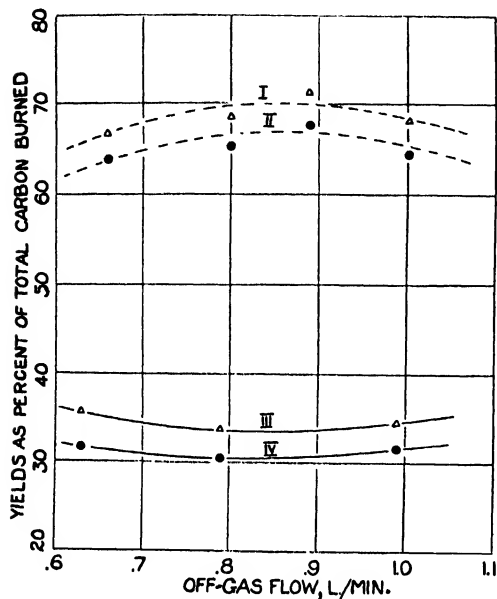
FIG. 6.   *Yields as a function of rate of flow of off-gas, from Table VIII.   I and II, total useful oxygen compounds and methanol respectively at a low oxygen concentration; III and IV, the same at a high oxygen concentration.*

Various Catalysts

Experiments in which the empty reactor and catalysts of glass, nickel-chromium steel, and silver were used are given in Table IX. The results of only two experiments in which the empty reactor was used are given, although a number were carried out. It was found difficult to obtain duplicates, the yield varying by about 50% in different experiments. Those listed are the experiments showing maximum yield. Because of the absence of any catalyst in the reactor, the free space was large, and the time that the gases were in the reactor was large. These conditions were shown to be unfavorable with natural gas (2), and the same conclusion may be drawn here. Good control evidently requires reasonable gas velocities and a small free space or large surface area or both. Experiments 159 and 161 may be compared to Experiments 156 and 153 of Table I in which copper was used. In this comparison it should be remembered that Experiments 159 and 161 were the most favorable of several, and the results could not be duplicated.

The experiments with glass and silver catalysts showed them to be as good as copper, a surprising result with glass at least. It was expected in view of the poor heat conductivity of glass that temperature control would be poor and the yields reduced. That glass was as good as copper may be seen by the results of Experiment 151 of Table II. It may be concluded that the reactions follow a different course over glass surfaces. Also, as an alternative, it may be suggested that reaction took place principally on the copper plated walls of the reactor, and the glass acted merely as a means of suppressing undesirable gas phase reactions.

TABLE IX

EXPERIMENTS USING THE EMPTY REACTOR AND CATALYSTS OTHER THAN COPPER AT 475° C.

Experiment No.	159	161	114	163	164
Catalyst			Glass	Steel	Silver
Pressure, atm.	141	141	184	141	141
Off-gas flow, litres/min	0.84	0.88	0.85	0.88	0.89
In-gas analysis:					
O_2	8.68	4.53	3.16	4.42	4.22
CH_4	55.2	73.8	80.2	74.3	74.3
N_2	36.12	21.68	16.64	21.28	21.28
Off-gas analysis:					
CO_2	2.02	1.00	0.37	1.05	0.68
O_2	0.11	0.03	0.18	0.0	0.18
H_2	0.97	0.87	0.0	0.82	0.66
CO	0.11	0.0	0.0	0.0	0.05
CH_4	58.3	77 5	82.0	78.0	77.9
N_2	38.49	20.58	17.34	20.13	20.53
$\dfrac{\text{Volume in-gas}}{\text{Volume off-gas}}$	1.09	1.06	1.04	1.06	1.07
Condensate, gm./100 litres in-gas at N.T.P					
Total	7.99	4.08	3.91	3.65	4.51
CH_3OH	1.23	1.20	1.71	1.03	1.25
CH_2O	0.0971	0 091	0.0644	0.0502	0.136
HCOOH	0.0586	0 0193	0.0305	0.0422	0.0254
H_2O	6.60	2.77	2.10	2.53	3.10
Alcohol in condensate, %	15.4	29.2	44.0	28.2	27.8
Total carbon oxidized, %	5.30	2.51	2.02	2.38	2.27
Yields, as % of total carbon burned to:					
CH_3OH	29.6	45.0	74.2	41.1	52.3
CH_2O	2.48	3 66	2.97	2.14	6.04
HCOOH	0.97	0.51	0 92	1.15	0.74
Total	33.05	49.17	78.09	44.39	59.08
Total inlet oxygen accounted for, %	78.0	70.0	78.5	67.5	77.5

The action of silver was not unexpected in view of its similarity to copper. It did not show visible signs of oxidation, as was always true of copper, but there was probably some adsorption of oxygen by the silver. The action of silver may be compared with that of copper by inspection of the results of Experiment 153, Table I. The only significant difference lies in formaldehyde production, silver producing about twice as much as copper. A greater activity on the part of silver, or the greater free space associated with the silver, would account for this greater degree of oxidation.

The steel catalyst was definitely poor in giving low yields and making control very difficult. This was expected in view of previous results (2) and also from the composition of the steel. While copper always showed evidence

of reaction with oxygen, the steel catalyst was unchanged before and after reaction. It showed no evidence of oxidation and reduction in that the surface was as smooth and bright after reaction as before. The steel was not inert, however, otherwise results similar to those found with glass would have been obtained. Evidently, the steel promoted complete oxidation.

Discussion

Inspection of the tables shows, on the basis of the carbon balance, an invariable loss of oxygen that ranges from 50 to about 10%. There is no relation evident between the oxygen loss and the conditions of the experiments. Further, in previous work (4), surplus oxygen was frequently found when natural gas was a reactant. Finally, in experiments at low temperatures where little reaction occurred, the oxygen balance was good. A search was made for an explanation of the oxygen balances. Obviously the catalyst might retain oxygen, and one reason for the use of glass was this possibility. However, the oxygen loss was as great with glass as with copper. Glass would not retain oxygen, and the copper walls of the reactor would not be expected to have more than a part of the capacity of the copper catalyst to retain oxygen. Similar remarks apply to the steel catalyst. The composition of the average gas samples was confirmed by analysis of instantaneous samples taken throughout an experiment. Further, the residual gas in the reactor after an experiment was withdrawn when the reactor was cool, and analyzed. The analysis agreed with that of the regular sample. The formation of gaseous oxygen compounds not detected in the methods of analysis used was highly improbable, but was examined. The off-gas was passed through a quartz tube maintained at 1100° C., a temperature high enough to destroy any compounds present with the production of carbon oxides and water. The oxygen content of the cracked off-gas was found to be the same as that of the off-gas itself. Confirmation of the methods of analysis of liquid condensates and off-gases by ultimate analysis has been mentioned. No solids or liquids were deposited in the reaction system. Impossible as it seemed, all the oxygen entering the system did not appear in the products. The only conclusion possible is that oxygen may be adsorbed, and possibly desorbed, in large amounts by the reactor, a conclusion that is questionable because of the large amounts of oxygen involved, and one that has still to be proved. Wiezevitch and Frolich (6) accounted for only 70% of the oxygen in experiments with natural gas and methane; with propane the recovery was only 40%. They offer no explanation.

Another observation with regard to oxygen should be pointed out. In nearly all experiments oxygen was found in the off-gases. This survival of oxygen was not expected, but was, nevertheless, real. Extreme care was taken in the sampling of the off-gases, and different methods were used, all with the same result—that oxygen survived. The only experiments where oxygen was absent in the off-gas consistently were those in which the empty reactor and steel as catalyst were used. This is suggestive in view of the lack

of control during such experiments, and suggests surface reactions under control as beneficial, and uncontrolled gas phase reactions going to completion as detrimental.

In view of the results presented in this and preceding papers (2, 4), a discussion at this time of the mechanism may be profitable.   The general features of the results may be explained reasonably well by a mechanism involving features of the "hydroxylation" theory advanced by Bone (1) and a chain reaction theory advanced by Norrish (5).   Obvious confirmation of the truth of Bone's theory lies in the production of large amounts of methyl alcohol together with formaldehyde and formic acid in small amounts.   The dependence of yield on oxygen concentration and the necessity for high pressures are details explicable on the theory.   Finally, tests for peroxides were always negative.

Bone's theory does not offer a satisfactory explanation, however, for many observations regarding the minor products of the reaction and the kinetics of the reaction.   It is believed that Norrish's theory clears up many of these points, and the following theory, combining aspects of both, is presented.

The primary reactions suggested are two, a surface reaction between methane and oxygen and a homogeneous gas phase reaction between methane and oxygen.   Both reactions require activated oxygen; in the first, the oxygen may be absorbed on the catalyst surface or combined with the catalyst, for example, as cuprous oxide, and in the second, the oxygen may be activated or in the atomic form.   The source of the atomic or activated gaseous oxygen will be discussed later.   The surface reaction may be written as:—

$$CH_4 + O_2 \longrightarrow CH_3OH \tag{1}$$

or

$$CH_4 + Cu_2O \longrightarrow CH_3OH + 2Cu.$$
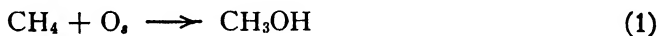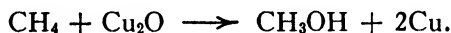
The methanol may survive or proceed to formaldehyde or formic acid by Bone's mechanism through further oxidation.   This reaction is required by Bone as the first stage in the oxidation of methane, and moreover it is admitted by Norrish as a reaction that occurs; according to Norrish's theory it plays the role of a chain breaker.   The homogeneous reaction may be taken from Norrish as:—

$$CH_4 + O^+ \longrightarrow CH_2: + H_2O \tag{2}$$

$$CH_2: + O_2 \longrightarrow CH_2O + O^+ \tag{3}$$
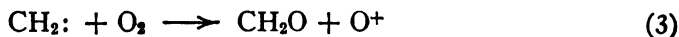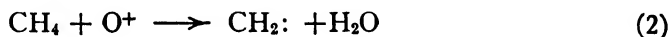
a chain reaction that is broken by (1) above.   The occurrence of the following reactions may be postulated also:—

$$n\ CH_2: \longrightarrow (CH_2)_n \tag{4}$$

$$CH_2O \longrightarrow CO + H_2 \tag{5}$$

or

$$CH_2O + \tfrac{1}{2}O_2 \longrightarrow CO + H_2O \tag{6}$$
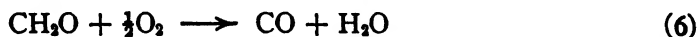
all of which are known to occur in other work.

Low oxygen concentrations favor methanol production, and one may conclude this from Reaction (1). This is only to be expected since with a limited supply, and a good catalyst, most of the oxygen in the reactive form will be on the catalyst. The methanol formed will survive in large part; to undergo further oxidation it would have to compete for oxygen with the much larger quantity of methane present. However, at high oxygen concentrations a considerable amount of activated oxygen may be expected in the gas phase. Methanol might be expected to oxidize further, the whole Bone series of reactions moving further toward carbon monoxide, carbon dioxide, and water.

A further and probably more important effect of high oxygen concentrations will be the promotion of the reactions in Norrish's theory, Reactions (2) and (3). These are homogeneous reactions and should be promoted by increased oxygen concentration in the gas phase, whereas Reaction (1) is heterogeneous and relatively independent of oxygen concentration once the catalyst surface is covered. Hence one might expect an increased production of aldehydes and higher hydrocarbons, Reaction (4), at high oxygen concentrations. However, aldehydes are very reactive compared to alcohols and hydrocarbons, and little would survive. Rather, an increased production of carbon monoxide, carbon dioxide, and water would result. In the methane experiments, the reduction in methanol yield, the production of carbon monoxide, and the increased traces of higher hydrocarbons at high oxygen concentrations is explicable on this basis. At low oxygen concentrations methanol is the primary product, and the amount of aldehyde formed is so small as to give no carbon monoxide. Reactions (3) and (4) are nearly, if not entirely, suppressed under these conditions. The occurrence of explosions at the highest oxygen concentration used is readily explained by Norrish's theory through the formation of aldehydes in large amounts. The reactive nature of the aldehyde, compared with methanol and methane, would account for the explosions.

To summarize,— it is postulated that two primary reactions occur, (1) and (2) above, the first being heterogeneous and desirable, and leading to the Bone mechanism of oxidation, the second being a homogeneous chain reaction yielding formaldehyde and gases but no methanol, and so undesirable. The relative proportion of each in the whole reaction depends mainly upon oxygen concentration, the proportion of the second increasing with increasing oxygen concentration.

Increasing the pressure of the reactants would affect the two reactions. With increasing pressure, Reaction (1) should be promoted through increased velocity and shift in equilibrium. Moreover, further reactions in the Bone series would be suppressed. However, the pressure of methane only would be effective, the effect of increased oxygen pressure being small, on the assumption that the catalyst is practically saturated with oxygen at all concentrations. Reactions (2) and (3) will be increased in velocity by increase in pressure or concentration of both methane and oxygen, with oxygen probably the more important reagent. These are detrimental reactions. The observed

result at low oxygen concentrations that there is a maximum in the pressure-yield relation follows from the above theory. As the pressure is raised at constant oxygen concentration, Reaction (1), the predominating reaction, and, at the same time, Reactions (2) and (3), are promoted. It is conceivable that the velocities of Reactions (2) and (3) increase more rapidly with pressure than does that of Reaction (1), the velocity depending on two reactants in the former case as against one reactant in the latter. Ultimately, and presumably at pressures higher than 184 atm. for the experiments in question, Reactions (2) and (3) predominate, and the yield of methanol falls. As the oxygen concentration in the gas is increased, the effect of pressure should change, Reactions (2) and (3) being favored at the expense of Reaction (1), and ultimately a decrease in pressure should favor Reaction (1). This was found to be the case at concentrations of 8 to 9% oxygen where the minimum pressure of 141 atm. gave the highest yield of methanol.

The effect of temperature is more or less obvious. Once the ignition temperature is reached, the effect of increased temperature is to increase the velocity of all reactions, the secondary reactions in both mechanisms as well as the primary. At sufficiently high temperatures, depending on the oxygen concentration, the oxidation and decomposition of the primary products, methanol and formaldehyde, to carbon monoxide, carbon dioxide, and water will be so extensive as to result in a decrease in yield. This has been observed, the optimum temperature being nearly independent of pressure but dependent on oxygen concentration.

The effect of space velocity on the reactions is not so clear. One might say at first sight that increasing rate of flow should result in increased yields of the primary products, but such was not the case. The conclusion to be drawn is that within the range of space velocity used, the reactions were always complete, or there was no time for further reaction. Neither methanol nor formaldehyde is stable with respect to the decomposition products, carbon monoxide and hydrogen, especially formaldehyde under the conditions used. However, the methane equilibrium, as well as the methanol equilibrium, with carbon monoxide and hydrogen will be set up, and in the presence of an excess of methane the whole system will shift toward methanol, a conception that may explain the survival of methanol independently of the time of contact. None of the catalysts are good catalysts for the methanol synthesis at high pressures, although copper is an excellent promoter of good catalysts. The alternative conception is that in the range of space velocities used, insufficient time was allowed for decomposition of methanol. Both conceptions may play a part. The low yield found in experiments with the empty autoclave is explicable on the basis of both space velocity and Norrish's chain reaction. The space velocity was much smaller in these experiments, and the time required for methanol decomposition may have been reached. The more likely explanation of the low yield, however, is the predominance of Reactions (2) and (3) through the large gas phase in the empty autoclave, with subsequent decomposition of the aldehyde formed.

While the action of catalysts has been discussed in part, some further remarks regarding the effect of glass and alloy steel may be of value in the light of the above-described mechanism. The inaction of alloy steel may be attributed to its failure to absorb or combine with oxygen to any extent. This alloy, of the stainless type, is characterized by its resistance to oxidation. Consequently only the copper walls of the reactor would promote Reaction (1), Reactions (2) and (3) taking place in the gas spaces between the steel chips. There would be a consequent fall in yield, as was observed.

The reason for the efficiency of glass as a catalyst is not clear. One can suggest that it is a good catalyst for Reaction (1) either through the adsorption of oxygen or methane, which is unlikely, or through some power of activation of the reactants. It is interesting to note that in the work of Bone and collaborators on the oxidation of methane at atmospheric pressures, surfaces such as porcelain, silica, or glass were the most effective in promoting aldehyde formation. The assumption made by Bone was, of course, that methanol was the primary product. As an alternative, it may be suggested that the glass was not a catalyst at all but served the purpose of a deactivator of oxygen, and broke the chains efficiently in Norrish's reaction. Consequently, the predominating reaction would be the formation of methanol on the copper walls of the reactor.

The efficiency of silver may be attributed to the same property effective with copper, namely, its ability to adsorb oxygen and its ease of oxidation and reduction. The greater solubility of oxygen in silver, with the possibility of a higher active concentration in the surface, may account for the increased formaldehyde production. Methanol may be oxidized to formaldehyde, or active oxygen may be liberated from the silver; this would promote Reactions (2) and (3).

In regard to experiments with natural gas (4), the behavior of ethane is of interest. Sometimes all or nearly all the ethane disappeared, the amount of methanol produced comparing with the amount of ethane oxidized and frequently being greater. More interesting however are those experiments in which the amount of ethane in the off-gas was nearly the same as that in the in-gas. Connected with the ethane is the reduction in temperature of the reaction when natural gas was used. Ethane appeared to promote oxidation of the methane at temperatures lower than normal. The oxidation of ethane may be considered to proceed according to the following mechanism:—

$$CH_3 - CH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_3 . CH_2 . OH$$
$$+$$
$$O_2$$
$$\downarrow$$
$$CH_3 . CHO + H_2O$$

$$+\tfrac{1}{2}O_2 \swarrow \qquad\qquad \searrow$$
$$CH_3OH + CO \qquad\qquad CH_4 + CO$$
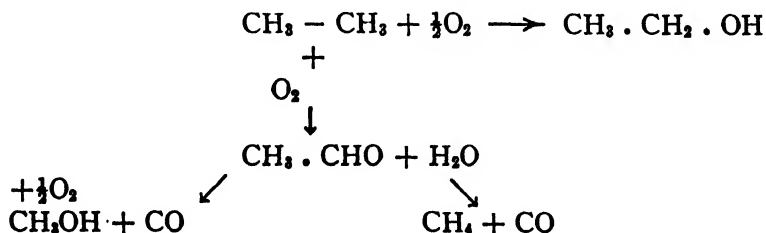
Between ethane and acetaldehyde, an intermediate stage analogous to Reaction (2) in Norrish's theory may intervene. The condensates from the natural gas experiments showed traces of ethyl alcohol by the iodoform test; this confirmed at least one reaction. No ethyl alcohol could be detected in the condensates from the methane experiments. The formation of acetaldehyde with its subsequent oxidation to methyl alcohol will explain the observed results that frequently the ethane burned could account for most of the methanol formed. The oxidation of the methane at low temperatures may be accounted for by assuming the decomposition of acetaldehyde to produce activated molecules, the methane being able to react directly with the oxygen and the carbon monoxide to activate other methane molecules. Alternately, as in Norrish's theory, we may assume the formation of free radicles from the ethane which are able to activate either methane or oxygen. Those experiments in which the ethane apparently survived are explicable on the basis of free methylene groups formed according to Reaction (2) of Norrish's mechanism. They will polymerize as in Reaction (4), and may be hydrogenated with the formation of ethane. More probable is the formation of cyclopropane, a fairly stable hydrocarbon easily mistaken for ethane in the methods of gas analysis used. While all gas analysis combustions were performed in duplicate and checked, the small amounts of higher hydrocarbons above methane found could easily have been ethane or cycloparaffins. The method of calculation, based on a small difference in large quantities, was such that ethane would not be distinguished from cyclopropane in the gas. The presence of higher cycloparaffins would interfere with the carbon monoxide and hydrogen determinations, and may account for the difficulties of analysis found with some of the natural gas experiments.

Finally, the bearing of the results on the utilization of natural gas may be discussed. The yields of methanol obtained, 75% as a maximum on the basis of carbon oxidized, are high, and can without doubt be raised. However, the conversion of total carbon in the system to methanol is very low, and probably not of commercial value even in a circulatory process. Further experiments in which oxygen in place of air is used are in progress, and they give results comparable to those found with air. Attempts to suppress the undesirable reactions occurring at high oxygen concentrations and the use of a circulatory process are in preliminary stages. At least 5% of the ingoing carbon, and preferably more, converted to methanol with high efficiency per pass is necessary to give the process practical possibilities.

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DERIVATIVES OF SUBSTITUTED SUCCINIC ACIDS

III. THE ACTION OF ALKALINE SODIUM HYPOBROMITE ON PHENYLSUCCINAMIDE AND αα'-DIMETHYLSUCCINAMIDE[1]

BY JOHN A. McRAE[2], ARTHUR W. WESTON[3], AND CHARLES F. HUBBS[4]

Abstract

Previous work on the action of alkaline sodium hypobromite on αα'-diaryl-succinamides has been extended to include phenylsuccinamide and αα'-dimethyl-succinamide, typical respectively of monoaryl- and αα'-dialkyl-succinamides. Phenylsuccinamide and sodium hypobromite give β-ureidophenyl-propionic acid and phenyldihydrouracil, but no phenylacetic acid. Likewise dimethylsuccin-amide gives dimethyldihydrouracil and no isobutyric acid. Hence the rearrange-ment observed with diarylsuccinamides does not occur with these two amides.

Introduction

Amides of the succinic acid type have been found to act in two different ways toward alkaline sodium hypobromite in the Hofmann reaction. Thus while succinamide and methylsuccinamide (9) give dihydrouracil and methyl-dihydrouracil respectively, diphenylsuccinamide (6), and p-methyl-, p-chloro-, and p-bromo-diphenylsuccinamide (5) give p-diphenylacetic acid and p-methyl, p-chloro- and p-bromo-diphenylacetic acid respectively. It has seemed desir-able to study the behavior of other differently substituted succinamides to ascertain the effect that substituents have in modifying their behavior in the Hofmann reaction. In the present paper a report is made on the action of sodium hypobromite on *phenylsuccinamide* as typical of monoarylsuccinamides and on dimethylsuccinamide representing αα'-dialkylsuccinamides.

Both of these amides behave much like methylsuccinamide in the Hofmann reaction. However, instead of 6-phenyldihydrouracil we obtained, from phenylsuccinamide, β-ureidophenylpropionic acid, $C_6H_5 . CH(NH . CONH_2) . CH_2 . CO_2H$, which was identified by direct comparison with a sample of this substance made according to the modification of Fischer's method used by Evans and Johnson (3). It was identified further by con-verting it into phenyldihydrouracil, again using an authentic specimen for comparison. In one experiment on phenylsuccinamide in which conditions were varied slightly, the action of the hypobromite produced phenyldihydro-uracil directly. Before isolation of the β-ureidophenylpropionic acid, steam was passed into the acidified solution for some time, and the distillate examined for phenylacetic acid. No trace of this acid was observed and consequently there was no indication that rearrangement had occurred. By the action of sodium hypobromite on phenylsuccinamide conceivably 5-phenyldihydrouracil and the corresponding acid, α-ureidomethyl-phenylacetic acid, $C_6H_5 . (NH_2 . CONH . CH_2) . CH . CO_2H$, might have been formed, but neither of these substances was isolated.

Cis-$\alpha\alpha'$-dimethylsuccinamide under the same treatment gave *5,6-dimethyl-hydrouracil*, as shown by a direct comparison with a specimen of this substance made by the application of the general directions of Fischer and Roeder (4) to tiglic acid with which it was found to be identical. As in the previous instance, steam distillation following acidification of the reaction mixture gave no trace of isobutyric acid, which would have been formed had a rearrangement occurred similar to that observed with diarylsuccinamides.

Phenylsuccinamide was made by the action of ammonia either on methyl phenylsuccinate, a reaction that takes place very slowly, or on phenylsuc-cinimide, which is the method to be preferred. Although Morrell (7) found that succinyl chloride and ammonia gave extremely poor yields of succinamide, it was hoped that the action of ammonia on phenylsuccinyl chloride would prove a rapid method, but using a variety of conditions only very small yields of phenylsuccinamide were obtained. Unsuccessful efforts were made to convert the product formed by the addition of hydrogen cyanide to ethyl α-cyano-β-phenylacrylate, presumably $C_6H_5CH(CN) . CH(CN)CO_2Et$, into phenylsuccinamide.

Authentic cis- and trans-dimethylsuccinamides were made first by Morrell (7) by the action of concentrated ammonia on cis- and trans-dimethyl dimethyl-succinates, but the reaction is very slow and the yields of the amides obtained are rather low. We found that by adding ammonia to dimethylsuccin-imide, filtering off the amide formed, evaporating to dryness, and again adding ammonia, finally an almost quantitative yield of the cis-amide could be obtained. After some preliminary experiments with other methods, that of Morrell was followed in making dimethylsuccinic acid according to Zelinski's procedure (10).

Experimental

PHENYLSUCCINIC DIAMIDE $C_6H_5 . CH(CONH_2) . CH_2 . CONH_2$

(a) From Dimethyl Phenylsuccinate

A mixture of dimethyl phenylsuccinate (10 gm.), dissolved in the minimum quantity of methyl alcohol (100 cc.), with 5 cc. of concentrated ammonia was allowed to stand for two weeks. The crystalline deposit which gradually formed was collected, and the remaining solution evaporated to dryness. The crystalline deposit and the latter residue were washed with acetone to remove unchanged ester. The amide thus obtained was recrystallized repeatedly from alcohol; m.p.* 211° C. Calcd. for $C_{10}H_{12}O_2N_2$: C, 62.50; H, 6.25; N, 14.58%. Found: C, 62.31; H, 6.35; N, 14.61%. The residual alcoholic liquors gave a small amount of material soluble in water. On acidification this gave a substance having on recrystallization the properties described by Anschütz (1) for the β-amide of phenyl-succinic acid, $C_6H_5 . CH(CO_2H) . CH_2 . CONH_2$; m.p. 145° C.

Melting points are uncorrected.

(b) From Phenylsuccinimide

Phenylsuccinimide was made either by distilling in a retort phenylsuccinic acid in a current of dry ammonia, or by heating ammonium phenylsuccinate under reduced pressure. The yield was about 70% by either method. Phenylsuccinimide (28 gm.) was dissolved in 50 cc. of concentrated ammonia. On standing for two days, phenylsuccinamide separated as a crystalline mass, and after filtration and washing with water to remove ammonium phenylsuccinate it was recrystallized from alcohol. The original ammoniacal mother liquor on evaporation gave a further quantity of the amide. Total yield: 18 gm. or 60% of the calculated yield.

(c) From Phenylsuccinyl Chloride

The chloride was made from phenylsuccinic acid and phosphorus pentachloride according to the directions of Anschütz (1). On adding slowly this chloride, with efficient stirring, to concentrated ammonia at $-10°$ C., a precipitate was obtained from which a small amount, namely 4% of that calculated, of phenyl succinamide was isolated. The principal products isolated were phenylsuccinic acid and the β-amide of phenylsuccinic acid; m.p. 145° C. Grinding the acid chloride with ammonium carbonate or adding it to dry ammonia dissolved in dry ether gave no better results.

Action of Sodium Hypobromite on Phenylsuccinamide

Phenylsuccinamide (6.9 gm.) made into a thin paste with 100 cc. of water was added slowly with efficient stirring to a sodium hypobromite solution made from 20 gm. of caustic soda in 100 cc. of water and 16 gm. of bromine. The temperature was maintained at $-5°$ C. during the addition of the amide, and it was then allowed to rise to room temperature; 12 gm. of caustic soda was then added and the mixture heated to 75° to 80° C. on the water bath for three hours. Contrary to the behavior of diphyenylsuccinamide, no ammonia was evolved. The alkaline solution was extracted with ether, but after removal of the ether from the extract nothing remained. Acidification gave a mass of crystals (7.2 gm.) which proved to be β-ureido-β-phenylpropionic acid. Recrystallized repeatedly from either alcohol or water, the substance melted at 191° C., the value given by Posner (8) and by Dakin (2) and confirmed by Evans and Johnson (3). A mixed melting point determination with β-ureido-β-phenylpropionic acid made from urea and cinnamic acid caused no depression of the melting point. Calcd. for $C_{10}H_{12}N_2O_3$: N, 13.46%. Found: N, 13.76%. Equivalent calcd: 208. Found: 208. The product was identified by converting it into 6-phenylhydrouracil, the melting point after several recrystallizations, 217° C., agreeing with the figure given by Posner and by Dakin. Likewise, it did not depress the melting point of authentic 6-phenyldihydrouracil. In one experiment with phenylsuccinamide 6-phenyldihydrouracil was isolated as the principal product of the reaction.

Meso-α,α'-dimethylsuccinamide

Dimethylsuccinic acid was made according to the directions of Zelinski (10). It was converted into its ammonium salt, and this on heating at 200° to 220° C. in an atmosphere of dry ammonia gas gave the dimethylsuccinimide in 80% yield, as described by Zelinski and Krapivin (11).

Dimethylsuccinimide was converted into the amide by dissolving it in the minimum amount of concentrated ammonia and allowing it to stand for 24 hr. A quantity of amide had separated. This was filtered and recrystallized. The filtrate was evaporated to dryness and dissolved in concentrated ammonia. This on standing gave a further quantity of amide. The process was repeated several times. Ultimately an almost quantitative yield of the amide was obtained. Better results were obtained in this manner than by allowing the filtrate to stand. The amide on recrystallization melted at 244° C. with decomposition. Morrell describes the cis-form as melting at 244° C. The "cis-form" is obviously the meso-form. The same product was obtained in small yield from dimethyl dimethylsuccinate.

Action of Alkaline Sodium Hypobromite on meso-Dimethylsuccinamide

Dimethylsuccinamide (4.3 gm.) was treated with alkaline sodium hypobromite under conditions strictly parallel to those previously described for phenylsuccinamide. After the reaction mixture had been heated on the water bath, the solution was acidified and steam distilled. No isobutyric acid could be detected in the distillate. The residual solution was evaporated to dryness and the residue extracted thoroughly with hot alcohol. After evaporation of the alcohol a crystalline residue was obtained which was repeatedly recrystallized from alcohol; m.p. 204° to 205° C. It separated in shining plates. The substance did not depress the melting point of 5,6-dimethyldihydrouracil synthesized as described below. Calcd. for $C_6H_{10}O_2N_2$: C, 50.6; H, 7.04; N, 19.7%. Found C, 50.4; H, 7.25; N, 19.8%.

5,6-Dimethyldihydrouracil

The procedure of Fischer and Roeder (4) was applied to tiglic acid. Tiglic acid (10 gm.) was heated with 6.3 gm. of urea to 210° to 220° C. until foaming ceased. The brown melt was recrystallized from hot alcohol; this gave characteristic shiny mica-like crystals, m.p. 204° to 205° C. The yield, based on the tiglic acid used, was 32%. Calcd. for $C_6H_{10}O_2N_2$: N, 19.7%. Found: N, 19.9%.

Acknowledgment

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THE CATALYTIC DEHYDRATION OF ETHYL ALCOHOL BY ALUMINA. II.[1]

By W. A. Alexander[2], W. R. Horn[3], and L. A. Munro[4]

Abstract

The decomposition of ethyl alcohol by two different samples of commercial alumina at 318° and 450° C. has been studied. The effect of time or previous use of the catalyst on the course of the reaction has been examined at 300° and 318° C. It has been found that the course of the reaction changes with change in water content of the catalysts. For the particular alumina used, there is one optimum water content for the production of ether and another for ethylene. For catalysts initially high in water there is a change in the sense of the reaction with use. Ignited catalysts of zero water content are not inactive, but become less effective for dehydration; this favors the production of ether.

The effect of the water content of alumina gel on its efficiency as a·catalyst for the production of ether from ethyl alcohol has been reported previously (14). It was found in the above-mentioned investigation that at 250° C. ether only was obtained from initial dehydration runs on catalysts of the same origin but differing in water content. There was, however, a distinct optimum water content of the catalyst for this reaction.

Further work was undertaken to ascertain whether, at a higher temperature, the efficiency of the dehydration to ethylene was also dependent on the water content of the catalyst. It was also determined to ascertain whether, at some intermediate temperature at which both ethylene and ether are produced, the course of the reaction could be changed in favor of one or other of the products of reaction by change in water content of the catalyst.

Apparatus

The apparatus employed in this investigation was essentially similar to that used previously, except that an intermediate condensing worm cooled in ice was inserted between the furnace and the receiver that was cooled with solid carbon dioxide. This prevented the occasional clogging of the system by the freezing of the water produced by the reaction.

Commercial absolute alcohol was used. This had a refractive index of 1.3633 at 15° C. as compared with 1.3637 at 15° C. as given by Sanfourche and Boutin (18) for pure alcohol. The alumina used initially was the same as that employed in the previous work. The product was first dried at 110° C. for eight hours, and then broken up so as to pass through a 6 to 10 mesh screen.

Experimental

Activation of Catalyst

The gels were activated by heating a weighed amount of catalyst in an electric furnace for two hours, for the runs at 450° C., and for one hour for the lower temperature runs. The temperature was measured by means of a thermocouple and was maintained constant ($\pm 2°$) by hand regulation of the rheostats. A constant slow stream of nitrogen (1 cc. per sec.) was passed through the catalyst tube during activation and cooling, although it was found that doubling the rate of flow of the nitrogen did not appreciably affect the residual water content.

The literature contains numerous references to the temperature of activation, the assumption being that *this* is the factor which determines the activity of a catalyst. Identical catalysts are not always obtained, although the activation is carried out at the same temperature for the same time and with the same flow of nitrogen. The resulting catalysts may differ in water content and activity. In the writers' experience, the resulting water content is a better criterion of activity than the temperature of activation.

If the total water content of the gel (determined by "blasting" to zero water content over a Méker burner) and the loss in weight on activation are known, the residual water content may be calculated. In these experiments this residual water is expressed as percentage of the weight of the activated catalyst. The activation temperatures chosen were always higher than the reaction temperatures used. This limits the range of water content of the catalysts obtainable for the higher reaction temperature, since all but 5.5% of the water is removed by activation for two and a half hours at 450° C. (14).

Analyses

Ether in the distillate was determined by Kunke's method (10).

The volume of gas produced was measured by displacement of saturated brine solution. Analysis showed that it was almost pure ethylene, with 1 to 2% of hydrogen and a trace of saturated hydrocarbons.

Semi-quantitative tests for the aldehyde content of the distillate were made (2). Appreciable quantities were found in all cases. The values for the high temperature runs range from 0.4 to 1.0%, and for the low temperature runs, from 0.1 to 0.4%. Ipatieff (9, p. 69) states that aldehydes are produced as a result of the presence of oxygen in the system.

High Temperature Runs—450° C.

Alcohol (20 cc.) was passed over different catalysts having residual water contents varying from 0 to 5.5%. The duration of the runs was 75 min. The theoretical yield of 8.1 litres of gas was obtained with all catalysts. Second runs with the same catalysts gave identical results. It is obvious that at this temperature there is no optimum water content as there is in the low temperature dehydration. Ipatieff (9, p. 69), in his book which appeared since this work was completed, reports that 420° to 450° C. is the optimum temperature for the production of ethylene from ethyl alcohol when alumina is used, but that the reaction "begins at 360°".

Runs at Intermediate Temperature—318° C.

A series of catalysts ranging in water content from 0 to 14.7% were used for the runs at 318° C. Twenty-five cubic centimetres of alcohol were passed

TABLE I
RUNS AT 318° C.—B.D.H. ALUMINA

Tube, and Run No.	Water in gel, %	Activation temp., °C.	A Per cent ether in distillate	B Ethylene, litres	B/A, moles	$\dfrac{\text{Moles alcohol decomposed}}{\text{Moles alcohol supplied (S)}} \times 10^2$		
						A/S	B/S	$\dfrac{A+B}{S}$
5 A	14.7	318	4.6	0	0	5.7	0	5.7
B			7.8	0	0	9.7	0	9.7
6 A	10.0	350	6.9	0	0	8.6	0	8.6
B			2.1	0	0	2.6	0	2 6
7 A	7.9	380	1.6	0	0	2.0	0	2.0
B			1.4	0.20	1.2	1.7	2 0	3.7
8 A	4.2	410	6.9	0.60	0.7	8.6	5.9	14.5
B			1.4	0.58	3.5	1.7	5.8	7.5
9 A	5.4	400	13.5	1.05	0 7	16.8	10.4	27.2
B			13.6	1.10	0.7	17 0	10.8	27.8
10 A	3.2	500	1.3	1.58	11.4	1.6	16.0	17.6
B			2.4	1 59	6.2	3.0	16.0	19.0
11 A	1.2	605	2.9	2.88	10 9	3 6	28.0	31.6
B			2.4	2.15	8.2	3.0	21.0	24.0
12 A	0		1.8	1.19	5.6	2.2	12.0	14.2
B			1.9	1 30	6.0	2 4	13 0	15.4
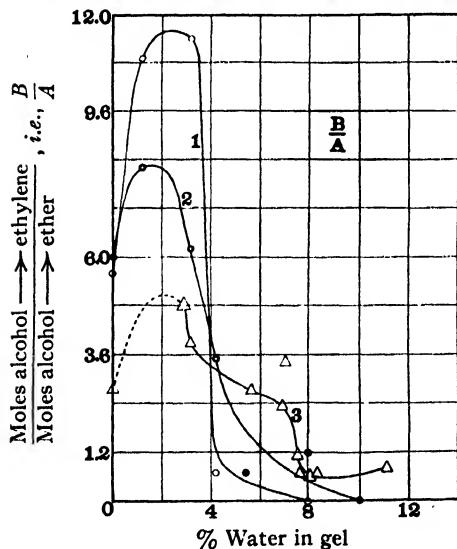
FIG. 1. *Course of reaction. Curve 1, B.D.H. alumina, A runs, 318° C. Curve 2, B.D.H. alumina, B runs, 318° C. Curve 3, St. L. I. alumina, A runs, 300° C.*

over the catalyst in 90 min. Two runs were made with each catalyst. The detailed results of these runs are given in Table I. The runs at 450° C. were carried out in tubes Nos. 1–4. Column six represents the ratio of the number of moles of alcohol decomposing to ethylene, to the number of moles of alcohol decomposing to ether. This is an index of the course of the reaction and is plotted in Fig. 1.

It will be observed that the course of the reaction changes with change in the water content of the activated catalyst, and further, that the ratio passes through a maximum for a water content of approximately 2% residual water. When the water content of the gel was greater, no

ethylene was produced, but the catalyst was still active for the production of ether (Fig. 2).

Columns 7, 8, and 9 in Table I show the molar efficiencies of the decomposition of the alcohol to ether, ethylene, and total dehydration, respectively. These are shown graphically in Figs. 2 and 3.
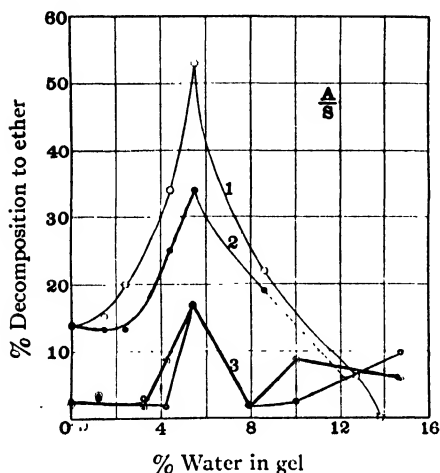
FIG. 2. *Efficiency of decomposition to ether. Curve 1, B.D.H. alumina, A runs, 250° C. Curve 2, B.D.H. alumina, B runs, 250° C. Curve 3, B.D.H. alumina, intermediate, A and B, 318° C.*
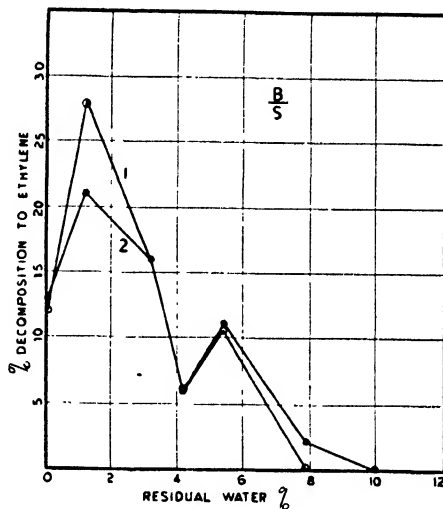
FIG. 3. *Change in efficiency of catalyst in the production of ethylene.*

In Curves 1 and 2, Fig. 2, the results obtained previously at 250° C. (14), when no ethylene was produced, are replotted as efficiencies for comparison with the present work. It will be noted that the optimum yield of ether occurs at the same gel water content.
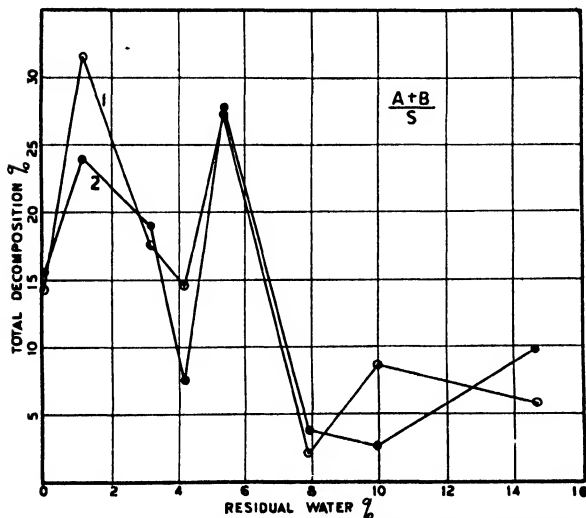
Fig. 3 shows the change in efficiency of the catalyst in the production of ethylene. Here optimum activity is reached at 2% gel water.

The variation of total catalytic activity with residual water is plotted in Fig. 4. This shows two maxima in the total reaction corresponding to those for ether and ethylene as noted above.

FIG. 4. *Variation of total catalytic activity with residual water.*

Variation in Efficiency with Use

It was noticed that an increased amount of ethylene was obtained from the second runs in Tubes 7 and 9 (Table I), and also an increased quantity of ether was obtained in several cases. This seemed to merit further investigation.

It would be expected that any change in catalytic activity with use would be most pronounced with gels of large water content. Activation can be considered, in part, as accelerated aging, and these gels have been activated (aged) to a lesser extent. There might also be some change in water content induced by use, even though the reaction temperature is lower than the activation temperature. Such a change would affect the course of the reaction as shown above.

Accordingly, two series of runs were made with Tubes 5 and 6 (Table I). The catalysts contained 14.7 and 10.0% residual water respectively. The results are given in Table II, where the headings of the columns have the same meaning as in Table I. The results are plotted in Figs. 5 and 6. It is evident from the figures that the indications of increased activity and change in the course of the reaction were realized in both cases.

TABLE II

EFFECT OF TIME OR USE—318° AND 300° C.

Tube, and water, %	Run	A ether in distillate, %	B Ethylene, cc.	B/A, moles	$\dfrac{\text{Moles alcohol decomposed}}{\text{Moles alcohol supplied } (S)} \times 10^2$		
					A/S	B/S	$\dfrac{A+B}{S}$
5	A	4.6	0	0	5.7	0	5.7
14.7	B	7.8	0	0	9.7	0	9.7
	C	1.9	290	1.2	2.4	2.8	5.2
	D	2.4	570	1.9	3.0	5.6	8.6
	E	3.3	580	1.4	4.1	5.7	9.8
	F	1.2	340	2.3	1.5	3.3	4.8
	G	1.1	380	2.8	1.4	3.7	5.1
	H*	0.5	80	1.6	0.7	1.0	1.7
	I*	0.9	70	0.8	1.1	0.8	1.9
	J*	0.5	70	1.3	0.6	0.8	1.4
6	A	6.9	0	0	8.6	0	8.6
10.0	B	2.1	0	0	2.6	0	2.6
	C*	1.8	110	0.5	2.2	1.1	3.3
	D*	0.7	120	1.4	0.9	1.2	2.1
	E*	0.6	100	1.3	0.7	1.0	1.7
	F*	0.9	100	0.9	1.1	1.0	2.1
	G*	0.4	80	1.7	0.5	0.8	1.3
	H*	0.3	140	4.9	0.4	1.8	2.2
	I*	0.16	120	6.4	0.2	1.3	1.5
	J*	0.4	90	1.9	0.5	1.0	1.5
	K*	0.7	90	1.1	0.9	0.9	1.8
	L*	0.8	90	0.9	1.0	0.9	1.9

* *Carried out at 300° C.*

The curve A/S for Tube 5 (Fig. 5, curve 1) suggests a periodic reaction. Periodic reactions have been observed in a number of catalytic decompositions, the explanation for which has yet to be found (12, p. 60). The evolution of ethylene by Catalyst 5 shows a decided maximum (Fig. 5, Curve 2). The
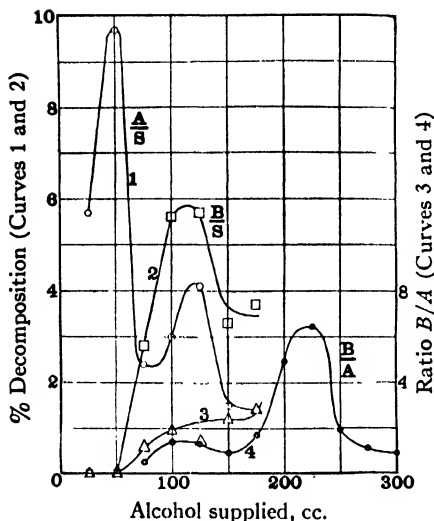
FIG. 5. *Change in sense of catalyst with use. Curves 1, 2 and 3, Tube 5, 318° C. Curve 4, Tube 6, 300° C.*
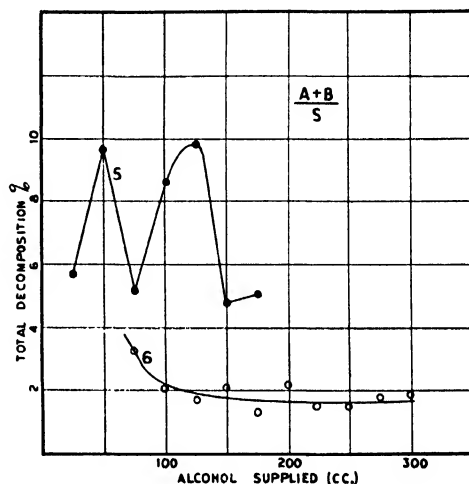
FIG. 6. *Total efficiencies of decomposition for Tubes 5 and 6.*

course of the reaction, given by the ratio B/A, is plotted in Fig. 5, Curves 3 and 4. The curve for Tube 6 shows a decided change in sense of the catalyst, with a subsequent return to the first ratios. The total efficiencies of decomposition for Tubes 5 and 6 are plotted in Fig. 6. Curve 5 shows evidence of a periodicity in the total reaction, while Curve 6 shows no such evidence. It is worth noting, however, that the proportion of molecules decomposing to ethylene has meanwhile passed through a maximum.

In a recent paper by Bliss and Dodge (4) the change in efficiency with use for the production of ethylene at 360° C. is shown for a number of alumina and mixed catalysts. In most cases a decrease in activity was observed, but with several catalysts an increase was found. No data are given regarding the initial water content of the catalysts.

A number of runs were made at 300° C. in which a sample of "Activated Alumina" supplied by the Aluminum Ore Co., E. St. Louis, Illinois, was used. Unfortunately this alumina was found to give so small a total decomposition (1 to 2.5%) that the accuracy of the observations was considerably decreased. The slight variation in total efficiency with changing residual water content is of doubtful significance. However, the ratio of the number of moles of alcohol decomposing to ethylene, to the number of moles of alcohol decomposing to ether, was evaluated, and is plotted in Fig. 1. The shape of the curve approximates that obtained with the B.D.H. sample of alumina, although the quantities involved are much smaller.

The inactivity of this catalyst is probably due to the presence of a small residue of alkali in the alumina (5).   A positive test with phenolphthalein was obtained when the alumina was boiled with water.   Bliss and Dodge (4) also record the very low efficiency of a commercial "active alumina" in the decomposition of alcohol.

Discussion

It is common experience that when the flow method is used it is difficult to obtain concordant absolute values for the products of reaction for duplicate runs.   Adkins and Lazier (1), who have drawn attention to this fact, point out that the ratio of the reactions was unchanged, that is, that differences in total activity did not affect the ratio of quantities of products.   The plot of this ratio, given in Fig. 1 for successive runs, shows definite agreement in change in the course of the reaction with gel water content and with time.

Sabatier and Reid (17) state that preparations of anhydrous alumina that have been heated to redness for a long time have almost no activity in the decomposition of alcohol, even at 420° C.   The catalyst with zero water content (Table I), obtained by blasting alumina over a Méker burner for 48 hr., showed a high total activity (Figs. 3 and 4).   While the total activity decreases as zero water content is approached, it does not fall to zero as would be expected from certain theories of catalysis (7).

The production of ethylene requires the elimination of one molecule of water from each molecule of alcohol, whereas in the formation of ether, one molecule is removed from two molecules of the alcohol.   The ratio of ethylene to ether, *i.e.*, the greater to the less dehydration, decreases from 2 to 0% water content (Fig. 1).

It seems to be the accepted idea that ignition produces sintering with a decrease in pore size (3).   It might be, however, that a fusion of finer pores would first occur.   This would decrease the available surface, but would actually result in a relatively greater number of large pores.   It is known that aging and heating produce increased size of pores in silica gel (13, p. 171), and it is to be expected that alumina would undergo the same change.   Bancroft and George (3) obtained a catalyst with large pores by heating the hydrated nitrate, and this preparation was the best dehydration catalyst.

Increase in the efficiency of dehydration with decreasing gel water content may be partly explained on the basis of the results of Bancroft and George. The persistent but decreased dehydration activity of the ignited (or blasted) samples may point to a decrease in the total number of these larger pores. It may be noted that the total activities of the B.D.H. alumina with zero water content were the same at 250° and 318° C.   This may be fortuitous, or may point to the same final gel structure in both cases.

There may also be several reasons for the change in the specificity of the catalyst with time.   First, it may be due to accelerated aging, in which case the effect would be greatest for gels of high water content.   This has been found to be true (Fig. 5).   Aging, as has been shown, will produce

larger pores, and this favors the production of ethylene. While the curves obtained with Tube 5 resemble those for the change in efficiency with decreasing water content, the curves obtained with Tube 6 show an almost constant total activity; this precludes activation by loss of water as the cause of changing activity. Second, it may be that the proportion of the reactants and products of reactants on the surface changes with time owing to sorption. There is probably an optimum distribution of reactant molecules on the surface of the catalyst for the production of ether, and another for the production of ethylene. Munro and McCubbin (16) found that there is an optimum adsorption ratio of reactants for the reaction

$$CS_2 + 2H_2O \longrightarrow CO_2 + 2H_2S,$$
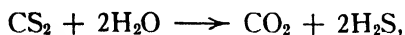
catalyzed by alumina. This adsorption ratio is probably an important factor in the change in catalytic activity with change in gel water content.

It has been shown that the amount of water unremoved by the activation of a given sample of alumina gel determines its adsorptive properties (15, p. 323) and catalytic activity, probably because the loss of gel water by heat treatment involves (1) increase in available surface, (2) change in porosity, and (3) in a measure, the extent of changes denoted by "aging", shown by several to involve also a change in X-ray patterns (22, 23).

Long, Frazer, and Ott (11) find that a relation exists between the arrangement of metal catalyst atoms in the crystal and the activity in promoting the reaction between hydrogen and benzene to form cyclohexane. These authors give several references to other papers indicating the dependence of catalytic activity and lattice dimensions. To these may be added papers by Eisenhut and Kaupp (6) and Storfer (20).

Wagner, Schwab, and Staeger (21), however, have shown that no change in crystal structure occurred with a promoted cupric oxide catalyst corresponding to its increase in activity. Smith and Hawk (19) investigated the crystal structure of oxide catalysts for the decomposition of methyl alcohol. They found no characteristic lines for their most active catalyst. Griffith and Hill (8) reached similar conclusions.

It has been shown that aluminas yield α-alumina on ignition. Preliminary X-ray studies on the writers' catalysts have not shown to what degree the crystal pattern of the gel fibrils is of importance.

Gels prepared by different methods being initially different in these several factors would not be expected to change in the same manner with loss of similar amounts of water. This aspect of the work is being investigated further.

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THE HEATS OF WETTING OF CELLULOSE BY ALCOHOLS AND THEIR AQUEOUS SOLUTIONS[1]

BY J. L. MORRISON[2], W. BOYD CAMPBELL[3], AND O. MAASS[4]

Abstract

The heats of wetting of dry cotton cellulose by several pure and aqueous alcohols have been measured for the first time. The rate at which the wetting occurred was also determined. The results indicate a preferential sorption of water from the aqueous alcoholic solutions. This conclusion is supported by similar measurements in experiments in which absolute alcohols were allowed to wet cellulose containing various amounts of previously adsorbed water.

Water adsorption by standard cellulose has been thoroughly investigated by Argue and Maass (1). They determined the heat of wetting by water of standard cellulose and such cellulose containing varying amounts of previously adsorbed water. The present paper describes an investigation of the adsorption of alcohols and aqueous alcoholic solutions under similar conditions.

So far as is known, the heats of wetting of cotton cellulose by pure alcohols have never been determined. Sheppard and Newsome (6) determined the heats of wetting of cellulose acetate by some alcohols and aromatic hydrocarbons. They found such values as 6.01 cal. per gm. for water, 7.52 for methyl, 5.65 for ethyl, and 4.94 for normal propyl alcohols, and 7.57 for benzene. The specific effect of the acetate groups in such measurements limits speculation as to the possible values for heat of wetting of cellulose itself by the same liquids.

A lone value for the heat of wetting of cotton by a 50% ethyl alcohol solution was reported by Chilikin (2).

Experimental Technique

The apparatus employed consists of a small rotating adiabatic calorimeter, the details of which have been described by Argue and Maass (1). The only change in procedure was the method of filling the inner calorimeter vessel with the dry cellulose. The cellulose after being placed in this vessel was dried in an oven at 100° C. in a stream of dried air. It was then transferred while hot into a metal container (containing phosphorus pentoxide) in the side of which

a rubber glove had been cemented. The greased lid could then be adjusted after the cellulose and its silver vessel had cooled down. A ground glass window sealed the top of the metal container.

The cellulose used in the present investigation was prepared by the method employed by Argue and Maass (1). Absolute methyl alcohol (Merck) and absolute ethyl alcohol were used without further drying. Absolute normal propyl and isopropyl alcohols were prepared from samples of 98 to 99% purity. These were refluxed over quicklime for four hours, distilled, and refluxed over magnesium metal for another four hours. Finally, they were distilled from the magnesium powder into dry vessels. Aqueous alcohol solutions were prepared from pure alcohols and distilled water. The percentage compositions were determined by density measurements, made with a hydrometer that measured specific gravity to within 0.002.

Results

The heats of wetting of standard cellulose by absolute methyl, ethyl, normal propyl, and isopropyl alcohols and several water solutions of these alcohols, are given in Table I. In the calculation of the heat evolved, it was necessary to correct for the evaporation of the vapors into the inner calorimeter. The partial vapor pressures and the heats of vaporization of each constituent, at 25° C., were used to make this correction (4, p. 290; 5, p. 138). Further, the best obtainable data on the specific heats of these solutions and pure substances were employed (3, 5, p. 116); in some cases interpolations of the data to 25° C. were necessary.

In Fig. 1 are plotted the data given in Table I. The data are given in mole percentage to facilitate discussion. Absolute methyl alcohol gives a value of 7.07 cal., which is comparable in magnitude to that for water, while the higher alcohols give values less than 1 cal. per gm. of cellulose. The order of the values is the same as the order of molecular weights of the wetting agents.

The quantities of heat evolved in the various methyl alcohol-
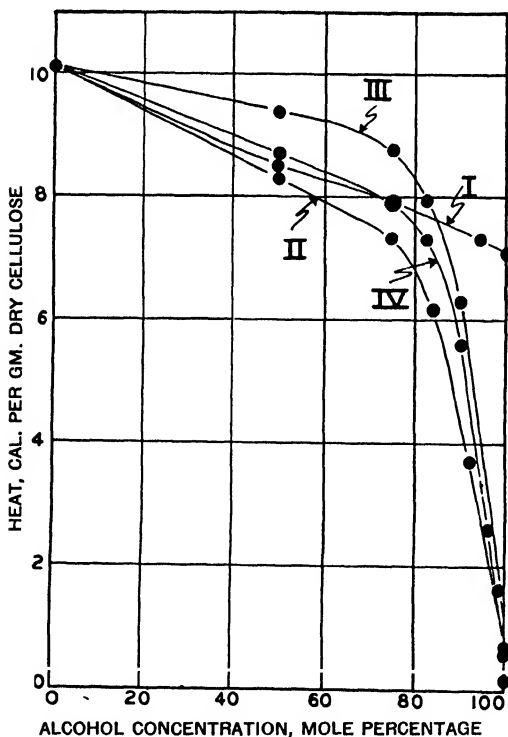
FIG. 1. *Heats of wetting of cotton cellulose by alcohol-water solutions. I, methyl alcohol; II, ethyl alcohol; III, normal propyl alcohol; IV, isopropyl alcohol.*

TABLE I

HEAT OF WETTING OF STANDARD CELLULOSE BY ALCOHOLS AND ALCOHOL-WATER SOLUTIONS

Alcohol	Concentration, mole % alcohol	Heat of wetting, cal. per gm. dry cellulose			
		Individual determinations			Mean
Methyl	100.0*	7.05	7.12	7.04	7.07
	94.4		7.36	7.26	7.31
	75.0		7.96	7.91	7.94
	50.0		8.49	8.51	8.50
Ethyl	100.0*		0.76	0.65	0.71
	92.6		3.71	3.64	3.68
	84.0		6.13	6.19	6.16
	75.0		7.31	7.42	7.36
	50.0		8.39	8.16	8.27
Isopropyl	100.0*		0.65	0.54	0.59
	96.5		2.57	2.59	2.58
	90.0		5.62	5.54	5.58
	82.5		7.38	7.23	7.30
	75.0		7.93	7.89	7.91
	50.0		8.73	8.65	8.69
Normal propyl	100.0*		0.14	0.18	0.16
	98.75		1.64	1.58	1.61
	90.0		6.22	6.36	6.29
	82.5		7.95	7.92	7.93
	75.0		8.74	8.78	8.76
	50.0		9.43	9.32	9.37

* *Absolute.*

water solutions give almost a straight line from 0 to 100% alcohol. The same is true for all the other alcohol solutions from 0 to 80 mole per cent of alcohol, the slopes over this range being such that normal propyl gives more heat than, isopropyl about the same heat as, and ethyl less heat than, do methyl alcohol solutions. For concentrations of alcohol from 80 to 100%, all but methyl give greatly decreasing heats of wetting, until, at a concentration of 100% alcohol, they give values less than 1 cal. per gm. of dry cellulose.

In conjunction with the above data is given the time to three-quarter value of the heat evolved, for virtually all these solutions, when they wetted the standard cellulose. No values are given for absolute ethyl, normal propyl, and isopropyl alcohols, the heat values themselves being so small that a time curve was difficult to even estimate. The time values were obtained by plotting the temperature difference from the initial temperature (ohms in this case) against the observed time after initiating the wetting process (by starting rotation). The final temperature reading minus the initial temperature reading, allowance being made for heat of rotation, is taken as the total heat of reaction, and the time to three-quarters of this temperature change is taken as the time to three-quarter value of the heat evolution. The equation

$$\text{Heat}_{(final)} - \text{heat}_{(time\ t)} = K \log t,$$

was found to hold fairly well, and the times to three-quarter values may be considered as a measure of the reaction velocity constant.

The results of the time values are given in Table II and Fig. 2. They can be considered as a measure of the time required to totally wet, so far as is possible, the cellulose.

TABLE II

TIME TO THREE-QUARTER VALUE OF THE HEATS OF WETTING OF STANDARD CELLULOSE BY ALCOHOL-WATER-SOLUTIONS

Alcohol	Concentration, mole % alcohol	Time to three-quarter-value, min.	Alcohol	Concentration, mole % alcohol	Time to three-quarter-value, min.
Methyl	100.0*	4.7	Isopropyl	96.5	10.7
	94.4	4.2		90.0	9.0
•	75.0	3.4		82.5•	5.8
	50.0	3.3		75.0	5.0
				50.0	3.8
Ethyl	92.6	14.0			
	84.0	7.7	Normal propyl	98.75	14.0
	75.0	4.9		90.0	6.8
	50.0	3.5		82.5	5.3
				75.0	4.8
Water		3.1		50.0	4.0

* Absolute.

FIG. 2. *Time to three-quarter value for the heats of wetting of cotton cellulose by water-alcohol solutions. I, methyl alcohol; II, ethyl alcohol; III, normal propyl alcohol; IV, isopropyl alcohol.*

Absolute methyl alcohol required one and one-half as much time as water, but the other alcohols require much longer times, to wet the cellulose. Especially is this so with ethyl alcohol. Solutions of the alcohols higher than methyl in the series begin to show rapidly increasing time for wetting at approximately 75 to 80 mole per cent alcohol. This is interesting, as it will also be observed that the values for the heat of wetting for the same solutions begin to decrease rapidly at this concentration.

Several desorption experiments were carried out. Standard cellulose was allowed to absorb definite amounts of water up to 7 or 8% moisture content.

.The samples so treated were placed in the inner container of the calorimeter, the lid was adjusted, and a weighed amount of absolute ethyl, normal propyl, or isopropyl, alcohol was placed in the calorimeter proper. Rotation caused contact of the moist cellulose with the absolute alcohol. With virtually all the alcohols a definite cooling took place, the amount depending on the original moisture content of the cellulose. The results of these experiments are given in Table III.

TABLE III

HEAT OF REACTION OF ABSOLUTE ALCOHOLS ON CELLULOSE CONTAINING ADSORBED WATER

Alcohol (absolute)	Moisture content, % dry cellulose	Heat evolved, cal. per gm. cellulose
Ethyl	6.34	−2.48
	6.25	−2.42
	3.83	−2.00
	1.60	−0.49
	0.41	+0.23
	0.00	+0.71
Normal propyl	7.45	−5.06
	2.66	−2.35
	0.00	+0.16
Isopropyl	6.50	−5.56
	2.80	−2.52
	0.00	+0.59

Discussion

The heats of wetting of cellulose by the pure liquids are in the order:— water, then methyl alcohol with a relatively small difference between these two, followed by a big decrease to ethyl, isopropyl, and finally normal propyl alcohol. The values for the last three are of a similar small magnitude. This is the order in which the heats might be expected to vary, but unfortunately data on adsorption of all these compounds by cotton are not available. When these are obtained, it will be of interest to compare molecular amounts adsorbed at the same relative humidity with the heats of adsorption and some of the known thermal constants of these compounds.

Aqueous solutions of methyl alcohol yield virtually a straight line relation for concentrations between 0 and 100% alcohol. The heats of wetting of water and of absolute methyl alcohol are of similar magnitudes. Hence, the affinities of cellulose for these two liquids are similar. Any mixture of the two would be expected to give an average heat of wetting that would depend on the relative amounts of each present; this is found to be true.

Further, the time for the wetting by methyl alcohol, though one and one-half as much as that by water, is quite comparable to the time for water. Solutions of methyl alcohol and water give intermediate values for the time, though there is some tendency for the time value for pure water to be approached quite rapidly.

Aqueous ethyl, normal propyl, and isopropyl alcohol solutions do not give a straight line relation between the quantity of heat evolved by the absolute alcohol and that by water. They behave similarly, however, in that from concentrations of 0 to 80 mole per cent alcohol, their solutions give a straight line relation of heat magnitudes, comparable to that for methyl alcohol

solutions. For concentrations greater than 80 mole per cent alcohol they all show low values of heat evolution. These facts require some explanation.

Consider a cellulose fibre wetted with an aqueous alcohol solution. The heat evolved by each constituent ought to depend merely on the volume, or perhaps on the mole per cent of each present. But this certainly is not the case for solutions of alcohols higher than methyl. In fact, a very low water concentration gives a quantity of heat considerably greater than that evolved by absolute alcohol. Certainly there must be a preferential adsorption of the constituent giving high evolution of heat; namely, water.

Probably at all concentrations there is some preferential adsorption of water at equilibrium. If the concentration of water in the alcohol is greater than 20 mole per cent, there is sufficient water immediately available for such equilibrium to be attained quickly. But if the water concentration is less than this, there is a time lag caused by the slowness of diffusion of the water to the cellulose surface. The effect is intensified as the proportion of water is reduced.

The possibility that water is preferentially adsorbed from the alcohol solution, at least for alcohols higher in the series than methyl, invites some further discussion. If water is preferentially adsorbed, then a process the reverse of solution in alcohol is occurring. These concentration changes should involve appreciable heat changes, which would be involved in the measurements of the heat of wetting of cellulose by the alcohol solution.

When ethyl alcohol is mixed with water at 25° C., heat is evolved over the whole range of concentrations (5, pp. 159, 160). Hence, the reverse process, namely, the removal of water from ethyl alcohol, would result in heat being absorbed (cooling). When water and normal propyl alcohol are mixed at 25° C., then over the range of concentration 35 to 100% alcohol, heat is absorbed (5, pp. 159, 160) (with ethyl alcohol the reverse is true). Therefore, on removing water from a normal propyl alcohol solution, heat evolution (warming) would occur.

Now consider the relative magnitudes of the heats of wetting of solutions containing the same mole percentage of these two alcohols. Normal propyl alcohol solutions give the higher values of the two; in fact, ethyl alcohol solutions give the lowest values of all. These facts definitely favor the assumption of a preferential sorption of water. They do not indicate which alcohol loses the most water. The fact that normal propyl alcohol solutions give higher values does not show that more water is sorbed from this alcohol, since the concentration change itself would cause a warming, while the reverse is true for ethyl alcohol. But some other evidence may indicate the relative affinities.

In the series, water, ethyl, and normal propyl alcohols, one would expect a greater affinity of water for ethyl than for normal propyl alcohol. Now if cellulose is added to these systems, it will sorb water from either alcohol— and probably more readily from normal propyl alcohol. The higher heats evolved by the normal propyl alcohol solutions would support this conjecture

if it were not for the interfering factor of concentration changes. However, the time curves definitely indicate that normal propyl alcohol solutions reach their final heat values sooner than ethyl alcohol solutions of high alcohol concentration. This would indicate that water is more readily removed from normal propyl alcohol; that is, the relative affinity of water for ethyl alcohol is greater than that for normal propyl alcohol.

For the present, some explanation has been offered for the observed phenomena when alcohols and alcohol-water solutions wet cellulose. Further speculations were made possible by the results of desorption experiments in which absolute alcohols were allowed to react with samples of cellulose already containing adsorbed water.

The data of these desorption experiments were given in Table III, and some very interesting calculations were made from these in combination with other data. The other data are heats of solution of water in alcohols (5, pp. 159, 160), heats of wetting of cellulose by aqueous alcohols (Table I), and Argue and Maass's heat of adsorption values of water by cellulose (1).

With these data it is possible to calculate the result of either of two processes that have the same initial conditions and should have the same final conditions by different sets of intermediate steps.

Consider a hypothetical three-compartment calorimeter. In one compartment is 1 gm. of dry cellulose, in another a small amount of water corresponding to the amount sorbed on cellulose in the desorption series, and in the third a fairly large definite amount of absolute alcohol.

Process 1

The water compartment is first connected with the dry cellulose. This would involve the evolution of heat as given by Argue and Maass's adsorption data (1, p. 568), in amount depending on the percentage of water relative to cellulose. Call this h_1.

Then allow the alcohol from the other compartment to make contact with the moistened cellulose. The heat evolved in this operation has been measured in the desorption experiments whose results are given in Table III. Call this heat h_2.

Now both water and alcohol are in contact with cellulose.

Process 2

The water and alcohol compartments are connected first. This causes the evolution of the heat of solution of the water in the alcohol, a value that may be obtained from the literature (5, pp. 169, 170). This may be called h_a.

Then permit the above mixture to wet the dry cellulose in the other compartment. The heat involved in this operation has been measured in the present work on heat of wetting as given in Table I, and it is called h_b.

Since the same final condition is reached from the same initial condition in the two processes, the net heat evolution should be the same in the two cases, *i.e.*,

$$h_1 + h_2 \text{ should } = h_a + h_b.$$

Table IV shows that such agreement is not obtained.

TABLE IV

CALCULATIONS CONCERNING TWO POSSIBLE PROCESSES

Original moisture content— % cellulose	Heats evolved, cal. per gm. of cellulose					Water, %
	h_1	h_2	h_a	h_b	$(h_1 + h_2) - (h_a + h_b)$	
Ethyl alcohol						
6.34	7.90	−2.48	0.49	1.00	3.93	2.20
6.25	7.87	−2.42	0.50	·0.94	4.01	2.26
3.83	6.19	−2.00	0.33	0.86	3.00	1.60
1.60	3.20	−0.49	0.15	0.76	1.80	0.92
0.41	0.95	+0.23	0.03	0.72	0.43	0.18
Normal propyl alcohol						
7.45	8.26	−5.06	−1.02	1.32	2.90	1.40
2.66	4.80	−2.35	−0.43	0.62	2.26	1.16

The heat evolved from Process 1 is always greater than that in Process 2, and some explanation of this is required.

Possible Explanations

(a) The heat of wetting of aqueous alcohol on cellulose, h_b, should be larger. In the case of Process 1, the water may open up a larger surface (making it available for wetting by the alcohol solution) than would obtain when the aqueous alcohol alone is initially wetting the cellulose as in Process 2. If reference is made to Table IV, it is seen that h_b for ethyl alcohol is 1.00 cal. for the sample containing 6.34% moisture, and, to account for the observed difference of 3.93 cal., an additional surface nearly four times as large as the existing one would have to be formed. This seems too large to be reasonable, though some such action may take place and partly account for the results.

(b) The value h_2 of Process 1 may be too small. It is quite evident that the cooling, when absolute alcohol is sorbed on moist cellulose, is due to a removal of at least some of the adsorbed water. It is possible that all the water may not be desorbed, and low values of h_2 may result.

If this explanation is correct, then a first approximation to the amount of water continuously held on the sample may be calculated by comparing the heat differences between the two processes with the heats of sorption found by Argue and Maass (1). A still closer approximation may be made by making due allowance for this in calculating corrected values of h_a and h_b. It is found that this correction is very small. The amount of water so calculated is shown in the final column of Table IV.

(c) It is possible that h_b is too small—but not for the reason put forward in Explanation *(a)*. Evidence has been given to show that water is preferentially sorbed on cellulose from aqueous alcohol solutions. The time curves seem to indicate that this preferential sorption is slow from alcohol solutions of low water concentrations. It is possible that water is not as completely sorbed as may be possible if infinite time were allowed. This would lead to low observed values of h_b.

At present, Explanation *(b)* seems more reasonable, but the question now arises as to the mechanism leading to the observed state of affairs.

The first thing that seems to come to mind is that it is a time effect, and that if infinite time were given, water could be taken away as in Process 1 and added, as in Process 2, until Process 1 = Process 2. If there is such a time effect then a similar consideration may apply to both Explanations *(b)* and *(c)*. In *(c)*, infinite time would allow more water to add on to the cellulose, and in *(b)*, the same would allow more water to be removed from the cellulose. It is possible that both *(b)* and *(c)* operate simultaneously, and that the two processes (1 and 2) would in time become equal. The final amount of water left on the cellulose would be some intermediate percentage, of the same magnitude whether the water was adsorbed or desorbed. The true equilibrium process would then be represented by some line intermediate between those for Processes 1 and 2 as given in Fig. 3.

This speculation has no experimental evidence to support it, because definite end values seemed to have been reached in reasonable times; and until some experiments are carried out in which measurements are made for hours or days, it cannot be proved.

Fig. 3. *Two processes for addition of water and ethyl alcohol to cotton cellulose. I, Process 1, (a) water plus dry cellulose, (b) then plus alcohol; II, Process 2, (a) water plus alcohol, (b) solution added to dry cellulose.*

Another mechanism is possible. Water may be able to enter places that alcohol cannot reach; and hence the water might be left there indefinitely. But, evidence from this laboratory seems to indicate that alcohol can replace all the water from cellulose if the alcohol is constantly renewed; it shows that

wherever water penetrates, alcohol also can, providing that water was there first.   Hence, it may be only a matter of waiting for diffusion to take place— this diffusion into the small interstices likely present in cellulose would require a long time.

Although the amount of water held by cellulose after alcohol contact (according to Table IV) is lower, almost in proportion to the amount originally present, no substantial conclusions may be drawn from this fact. These amounts are what might be expected as ordinary sorption phenomena, *viz.*, that there is an equilibrium between the amount of water sorbed on the solid and that in solution, and that the ratio of the water on the solid to that in solution is greater when the concentration is small.

Several possible explanations and mechanisms have been given for the anomalous results observed when alcohol is sorbed on moist cellulose.   The simplest one advanced, namely, that it is only a question of insufficient time being allowed for complete diffusion, may be the best explanation.   However, no attempt is being made to come to too definite a conclusion.

The evidence from the heat of wetting of cellulose by aqueous alcohols seems to indicate quite distinctly a preferential sorption of water.   The magnitude of the heat values and the time to reach those values both favor this conclusion.

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THE EFFECT OF SULPHITE LIQUOR COMPOSITION ON THE RATE OF DELIGNIFICATION OF SPRUCE WOOD AND YIELD OF PULP[1]

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Abstract

A technique has been devised for studying the delignification of wood in sulphite liquor under accurately controlled conditions. The rate of delignification of resin extracted spruce wood-meal has been determined at 130° C. over the concentration range 0.2 to 1.4% combined, and 2 to 14% total, sulphur dioxide. The reaction shows a systematic deviation from the first order relation that is the same for any composition of liquor. A quantitative relation between the rate of delignification and the concentration of free sulphur dioxide, or better, the partial pressure of sulphur dioxide gas, has been established. The nature and significance of this relation is discussed in connection with the mechanism of the delignification process. It has been shown that the hydrogen ion concentration alone does not determine the rate of cooking, but evidence is presented that indicates that the product of the concentrations of the hydrogen and bisulphite ions is the controlling factor.

The yield of pulp for any given lignin content is independent of the free sulphur dioxide over the whole concentration range, but increases in a marked manner with the concentration of the combined. An explanation is offered, and the practical aspects are pointed out.

Introduction

The question of liquor concentration is one of the most controversial in the sulphite industry (12). This is due to the fact that the effective liquor concentration in commercial cooks depends more on digester operation than on the initial composition of acid. None of the factors, temperature, pressure, or composition can be maintained constant, and it is therefore impossible to determine the actual relation of liquor concentration to the course of the cooking under mill conditions.

It is generally believed that an increase in free sulphur dioxide increases the rate of pulping, but that the combined sulphur dioxide, in excess of a certain minimum, is of little consequence (4, 14). Up to the present time, no quantitative relations have been established. Stangeland (18) made some small-scale laboratory cooks with constant combined, and different total, sulphur dioxide concentrations, but his results are difficult to interpret because he used low liquor ratios and measured the removal of "incrustants" rather than lignin. McGovern (13) made a series of semi-commercial cooks with liquor containing initially 1.2% combined, and 5 to 20% total, sulphur dioxide. He showed that the rate of cooking increased with the strength of the acid, but to a decreasing extent at the higher concentrations.

Miller *et al.* (14) maintain that the "excess" sulphur dioxide (total − 2×
combined) governs the rate of cooking. Gishler and Maass (5), on the other
hand, have shown, from a study of the equilibria existing in sulphite liquor,
that a complex ion corresponding to 2CaO to 3SO₂ might exist, in which case
the true free sulphur dioxide would correspond to the total − 1.5× combined.
Mitchell and Yorston (15) obtained some evidence in support of this view
by cooking resin extracted sawdust in various sulphite liquors. However,
insufficient data were obtained to make the results conclusive.

The object of the present investigation was to obtain reliable and com-
parable data on the effect of various constituents of sulphite liquor on the
rate of delignification and yield of pulp, under such exact conditions that
undesirable factors could be eliminated, and without the restrictions imposed
by commercial practice. Two purposes were in mind, *viz.*: first, to obtain a
quantitative relation between one or more components of sulphite liquor and
the rate of pulping, in order to help elucidate the mechanism of the delig-
nification reaction; and second, to determine the practical advantages of
cooking with different liquors, and to provide data for the more intelligent
study of sulphite pulping under commercial conditions.

Experimental

In order that interpretation of the results would be possible, it was necessary
to make small-scale cooks under conditions of constant temperature, pressure,
and concentration, and to eliminate the difficulties of penetration and diffusion
as much as possible. This was accomplished by using a high liquor ratio,
and by using wood-meal instead of chips. That these are conditions im-
possible in commercial practice, in no way invalidates the results.

The wood used for cooking was well seasoned white spruce of density 0.43.
It was ground and sieved to 40 to 100 mesh, and then the resin was extracted
with alcohol-benzene (1 : 2) for 12 hr. in a Soxhlet apparatus. It was then
air-dried and stored for use. The lignin content of the prepared meal was
27.5%.

Several preliminary series of cooks were made in the bronze bomb digesters
(200 cc.) used in previous investigations (3). However, it was found that
the rubber gaskets used in sealing the bombs were attacked by the liquor at
cooking temperatures; this resulted in appreciable loss of sulphur dioxide.
It was, therefore, necessary to devise a new method.

Pyrex bombs of 100 cc. capacity, 1⅜ by 5 in. with a neck ⅜ by 2 in., were
constructed. Six bombs were used for each run. Each bomb was charged
with 2 gm. of the wood-meal of a known moisture content. Sulphite liquor
of the desired concentration was cooled below 0° C. to minimize loss of sulphur
dioxide and injected into the bombs. Sufficient space was left to permit
expansion of the liquid at 130° C. Before the tips of the bombs were sealed,
the air was flushed out by a stream of sulphur dioxide gas. The liquor ratio
was about 50 : 1, ten times that used in commercial practice.

Each glass bomb was provided with an outer metal casing, capable of withstanding high pressures. The space between the bomb and the jacket was filled with water to reduce the pressure difference. The loaded bombs were dropped into a well stirred glycoline bath, preheated a little above 130° C., to allow for the cooling effect of the bombs. The temperature of the bath was then held constant at 130° C., which was the cooking temperature employed throughout this investigation. The bombs were placed on their sides in the bath to prevent accumulation of the meal at one end. At given intervals the bombs were removed from the bath and quenched in water.

After the bombs were cooled below 0° C., they were opened, and the liquor was analyzed immediately by the Palmrose method (16). In spite of the high liquor ratio, the concentration of lime and sulphur dioxide decreased slightly during cooking. Therefore, the mean liquor concentration was taken as the average of that for all the bombs in a given run, analysis being made after cooking. The cooked wood-meal was filtered, washed with tap water, oven dried, weighed, and analyzed for lignin. All lignin determinations were made by the Ross-Potter method (17), and all yields calculated on the resin extracted, bone-dry wood basis.

Correction for the Sulphur Dioxide in the Vapor Phase

As the bombs are heated to 130° C., some sulphur dioxide passes into the vapor phase; this reduces the concentration in the liquid. From a calibration of the bombs, the volume of both liquid and vapor phases at 130° C. could be calculated, allowance being made for expansion of the liquid. The partial pressure of sulphur dioxide for the desired concentration and temperature was obtained by extrapolating the data of Gurd, Gishler, and Maass (7). Thus the loss of sulphur dioxide from the liquid could be calculated and the analytical concentration corrected.

Correction for the Rate of Heating of the Bombs

The observed time of cooking was taken from the moment the bombs were dropped into the hot bath to the moment they were quenched in water. It became apparent, however, that for short, fast cooks, the time required for the bombs to heat up to 130° C. would introduce an appreciable error in the results. Previous investigators have made various rough estimates to correct for this error in timing, or have ignored it completely.

An indirect method was used to determine this correction accurately. One bomb and casing were both fitted with stems so that a thermometer could be suspended in the centre of the glass bomb, while the bomb was immersed in the oil bath. Actual heating curves were then obtained for the following:

(a) Bomb and casing filled with water at 20° C.; bath at 100° C.

(b) Bomb and casing filled with oil at 20° C.; bath at 100° C.

(c) Bomb and casing filled with oil at 20° C.; bath at 130° C.

With the bath at 100° C., the ratio of the times to a given temperature for *(a)* and *(b)* was approximately constant. Hence from *(c)* a fourth curve could be calculated:

(d) Bomb and casing filled with water at 20° C.; bath at 130° C.

This was considered sufficiently close to the actual conditions of a cook with sulphite liquor.

The calculated curve for *(d)* was exponential in shape, the temperature in the bomb rising rapidly at first, but more slowly as the temperature of the bath was approached. It was therefore necessary to determine the amount of cooking that took place during the heating period.

On the assumption of a temperature coefficient of the sulphite process of 2.0 per 10° interval, and a linear change in temperature, the following relation was derived:

$$\theta_1 = \int_o^t 2^{tx/10} dt \qquad \qquad (1)$$

where θ_1 = equivalent time of cooking at the initial temperature, T_1 ,

x = rate of heating, degrees per minute,

t = time of heating, minutes.

On integration, Equation (1) becomes

$$\theta_1 = \frac{2^{tx/10} - 1}{0.0693x} . \qquad \qquad (2)$$

It was desired to know the equivalent time of cooking at 130° C. (θ_2) for the heating period. This was obtained from the relation

$$\theta_2 = \frac{\theta_1}{2^{(130-T_1)/10}} = \frac{2^{tx/10} - 1}{0.0693x \cdot 2^{(130-T_1)/10}} \qquad \qquad (3)$$

Since the actual heating curve was exponential, it was divided into five approximately linear sections, and Equation (3) applied to each in turn. In this way, the amount of cooking done during the heating period was calculated in terms of the time required to do the same amount of cooking at 130° C. This is independent of the absolute velocity of delignification, and hence the same time correction can be applied to every cook. The time required for the bomb to reach 130° C. was calculated to be 35 min., and the amount of cooking done during this period was calculated from Equation (3) to be equivalent to 22 min. of cooking at 130° C. Therefore, the time correction is 13 min., or 0.22 hr., which is to be subtracted from the observed time the bombs were in the bath.

No correction was necessary for cooking taking place during cooling after removal from the bath, since the temperature of the bombs dropped so rapidly when quenched in water that cooking was almost instantly stopped.

Results

The data for a typical run are given in Table I to illustrate the calculations. The initial liquor concentration was about 0.5% combined, and 4.5% total, sulphur dioxide. Since some sulphur dioxide is lost in filling the bombs, only the final concentrations are averaged. Table I shows the small but

TABLE I

THE RESULTS OF A TYPICAL COOK (RUN No. 59)

Time in bath (uncorrected), hr.	Combined sulphur dioxide, %	Total sulphur dioxide (uncorrected), %	Total sulphur dioxide (corrected), %	Yield of pulp, %	Yield of crude cellulose, %	Lignin, % of pulp	Lignin, % of original wood
0				100	72.5	27.5	27.5
1.5	0.45	4.20	4.17	71.3	56.7	20.5	14.6
3	0.42	4.18	4.17	60.7	53.4	12.0	7.27
4	0.40	4.15	4.12	53.8	50.4	6.34	3.41
5	0.40	4.08	4.07	50.9	48.9	3.96	2.02
6	0.39	4.05	4.04	49.1	48.2	1.92	0.94
7	0.39	4.02	4.00	47.3	46.7	1.17	0.55
Average	0.41	4.12	4.10				
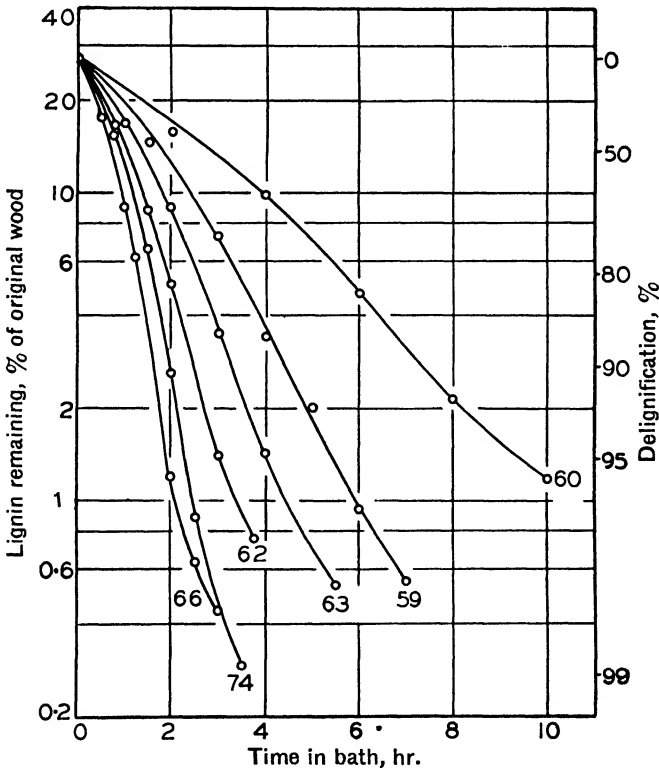
:. 1. *Effect of sulphur dioxide concentration on the rate of delignification of spruce wood*)° C. *Series B. Combined sulphur dioxide, 0.4%.*
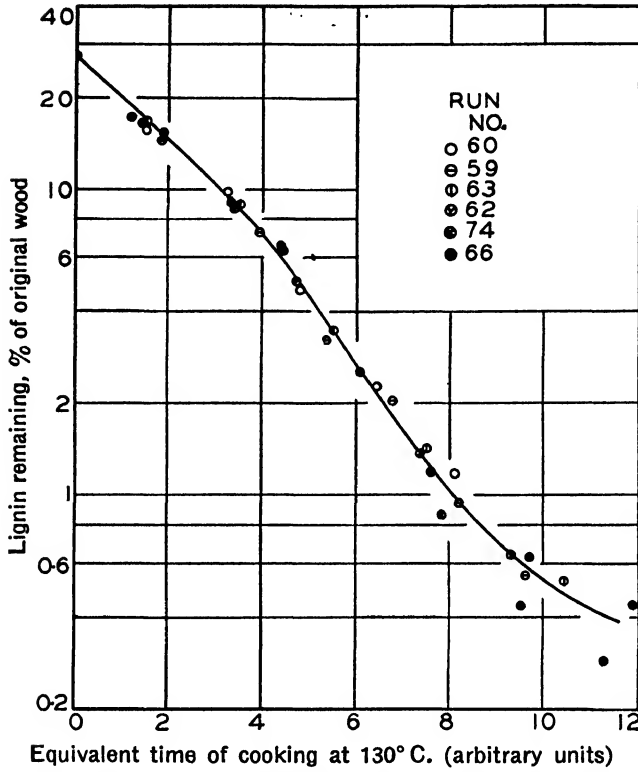
FIG. 2.   *Effect of sulphur dioxide concentration on the rate of delignification of spruce wood at 130° C.   Series B.   Combined sulphur dioxide, 0.4%.*
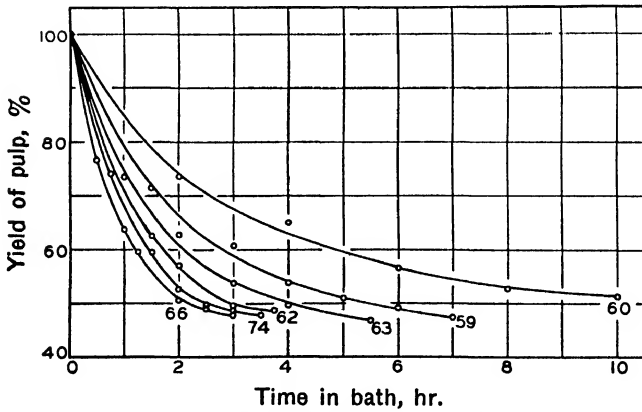
FIG. 3.   *Effect of sulphur dioxide concentration on the yield of pulp at 130° C.   Series B. Combined sulphur dioxide, 0.4%.*

regular consumption of lime and sulphur dioxide as cooking proceeds. In this particular run, the correction for loss of sulphur dioxide from solution is small, but with cooks at higher concentrations it becomes much more important.

The yield of pulp for Run No. 59 is plotted in Fig. 3, and the lignin as percentage of the original wood is plotted in Fig. 1 on a logarithmic scale. It is seen that the delignification curve deviates somewhat from the first order relation, and hence no attempt was made to estimate velocity constants. The time required to remove 90% of the lignin, as read from the curve, was taken as the best measure of the rate. The yield of pulp at any given lignin content is found by comparing Figs. 1 and 3.

A complete summary of all runs is given in Table II. The range of concentration covered was 0.2 to 1.8% combined, and 2 to 14% total, sulphur dioxide, limited only by solubility restrictions at 130° C. Use was made of

TABLE II

THE EFFECT OF SULPHITE LIQUOR COMPOSITION ON YIELD OF PULP AT 130° C.

Series No.	Run No.	Av. comb. sulphur dioxide, %	Av. total sulphur dioxide (corrected), %	80% delignification		90% delignification		95% delignification	
				Time (uncorr.), hr.	Yield pulp, %	Time (uncorr.), hr.	Yield pulp, %	Time (uncorr.), hr.	Yield pulp, %
A	75	0.16	1.70	10.15	52.5	13.50	49.0	17.5	45.7
	72	0.18	3.68	3.80	54.3	4.96	50.2	6.27	47.6
	71	0.18	5.07	2.90	54.1	3.63	50.2	4.75	47.6
	73	0.17	6.92	2.09	54.0	2.70	49 8	3.44	47.9
	Av.	0.17			53.7		49.8		47.2
B	60	0.39	2.57	5.62	57.8	7.48	53.5	9.45	51.0
	59	0.41	4.10	3.40	57.0	4.45	52.5	5.45	50.0
	63	0.40	5.59	2.55	57.5	3.26	52.3	4.05	49.4
	62	0.40	7.34	1.94	57.6	2.48	52.8	3.01	49.5
	74	0.41	9.67	1.61	57.8	1.97	53.1	2.27	50.7
	66	0.42	12.48	1.30	58.5	1.62	54.2	1.92	51.2
	Av.	0.40			57.7		53.1		50.3
C	56*	0.87	3.27	5.10	61.0	6.90	55.6	8.52	53.0
	51	0.91	4.14	3.90	60.8	5.30	56.0	6.60	53.0
	77	0.92	4.87	3.13	62.0	4.16	56.4	5.20	53.0
	76	0.91	5.88	2.50	61.0	3.26	56.1	3.95	53.4
	52	0.93	5.97	2.52	60.6	3.29	56.4	4.13	53.7
	53	0.91	8.05	2.02	60.2	2.50	55.9	3.10	52.7
	55	0.87	10.65	1.62	60.2	2.00	55.7	2.47	52.3
	61	0.92	13.92	1.22	61.0	1.59	55.9	1.88	53.1
	Av.	0.90			60.8		56.0		53.0
D	67*	1.44	7.68	1.97	63.5	2.53	57.8	3.00	54.8
	68	1.38	10.71	1.57	62.5	1.99	57.2	2.32	54.5
	69	1.39	14.04	1.31	63.0	1.65	57.5	1.92	54.6
	Av.	1.40			63.0		57.5		54.6
E	64*	1.76	11.38	1.45	64.3	1.82	59.0	2.20	55.6
	65*	1.84	13.46	1.27	64.5	1.68	58.5	2.05	55.0
	Av.	1.80			64.4		58.7		55.3

* Precipitation of calcium sulphite occurred.

the data of Gishler and Maass (6) on precipitation temperatures, to avoid precipitation of calcium sulphite during cooking.   Unfortunately, their temperatures were much too high, a fact that has since been confirmed by Beazley (1). 'Hence precipitation did occur unexpectedly in several runs (marked with an asterisk, Table II).   This made the true concentration at 130° C. uncertain in these cases.

The uncorrected times to 80, 90, and 95% delignification for each run were read from the delignification curves, which for Series B are plotted in Fig. 1. The yields of pulp at the corresponding times were read from the yield curves, which for Series B are plotted in Fig. 3.   The time correction does not affect the yields of pulp taken at a given lignin content.

All the delignification curves showed a similar, definite deviation from the straight line, first order relation.   This agrees with the results of Yorston (19) and Corey and Maass (3).   It was of interest to know whether the nature of this deviation varied with the liquor composition.   To make comparison between the curves in Fig. 1 possible, the time correction was first applied by subtracting 0.22 hr. from the observed times, and then each value was multiplied by the arbitrary factor $6/t_{90\%}$ to make the curves coincident.   The result is shown in Fig. 2, and it is seen that all the points fall on the one curve, irrespective of the composition of the liquor, except at low lignin values where analysis is less accurate.

Series A and C were calculated and plotted in the same way, with the same result.   The S-shape of Fig. 2 is quite pronounced, and evidently the mechanism of the reaction, whatever it may be, is the same with all liquors.   Increase in sulphur dioxide content does not alter the relative rates of the sulphonation and hydrolysis reactions, which might be expected if Hägglund's theory of sulphite pulping is correct (8, 10).

The Effect of Sulphite Liquor Composition on the Yield of Pulp

An inspection of Table II shows that the yield of pulp at a given lignin content increases rapidly with the combined, but is virtually independent of the total, sulphur dioxide over the whole concentration range.   This is brought out in Fig. 4, in which the yield is plotted against the combined sulphur dioxide for different lignin contents.

This effect of the combined sulphur dioxide on the yield is substantiated qualitatively by the results of Hägglund and Nihlen (11) and Mitchell and Yorston (15), although Miller *et al.* (14) state that they could not show any variation in yield attributable to any of the factors in acid composition. It has generally been believed that high sulphur dioxide content resulted in a loss in yield, owing to the greater acidity of the liquor.   The contradictions in the literature are no doubt due to lack of uniformity in the methods used and the fact that the yields, in some cases, were not taken at the same lignin content.

The effect of liquor composition on yield may be explained, on the assumption that cellulose degradation is proportional to the hydrogen ion concentration of the liquor at a given temperature.   For a constant free sulphur
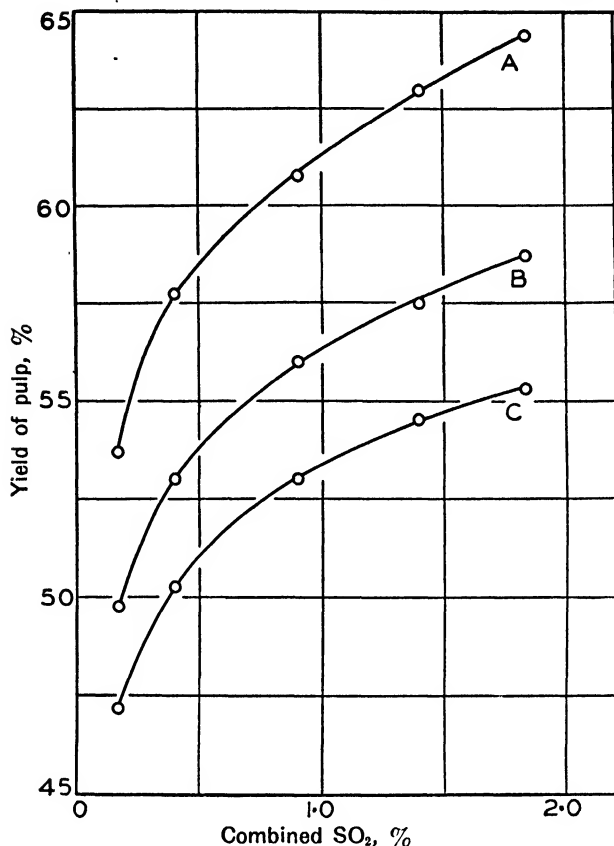
FIG. 4.   *Effect of combined sulphur dioxide concentration on the yield of pulp at 130° C.*
Delignification: A, B, C—80, 90, 95% respectively.

dioxide content, the pH of the liquor increases with the combined.   In fact the pH curves for sulphite liquors of different lime concentrations, obtained by extrapolating the data of Gishler and Maass (5) to 130° C., are almost identical in shape with the yield curves of Fig. 4.   That the yield should be independent of the total sulphur dioxide, even though the pH is not, is due to the fact that increased acidity is balanced by the decrease in time required for cooking.

It has thus been shown conclusively that, under the conditions of these experiments, increase in total sulphur dioxide will not affect the yield, whereas an increase in the combined sulphur dioxide greatly improves the yield. The yields obtained with the liquors containing 0.8% or more of combined sulphur dioxide are distinctly better than those realized in mill practice. It may be suggested that the lower yields under mill conditions are due to the low concentration of combined sulphur dioxide prevailing towards the end of the cook.   However, opinion is divided as to the effect of changes in the initial concentration of combined sulphur dioxide on the yield from a commercial digester.

The Effect of the Free and Combined Sulphur Dioxide on the Rate of Delignification

The free sulphur dioxide (total−combined) and the "excess" sulphur dioxide (total−2×combined) for each run were calculated and are shown in Table III. In Column 8 is given the corrected time to 90% delignification. The rate of delignification, then, is proportional to the reciprocal of this time and is given in the last column of Table III.

TABLE III

THE EFFECT OF SULPHITE LIQUOR COMPOSITION ON THE RATE OF DELIGNIFICATION OF SPRUCE WOOD AT 130° C.

Series No.	Run No.	Av. comb. sulphur dioxide, %	Av. free sulphur dioxide (total − comb.), %	Av. excess sulphur dioxide (total − 2×comb.), %	pH of liquor at 130° C.	Partial press. sulphur dioxide 130° C., cm.	Time to 90% delig- nification, hr. (corrected) $= t_{90\%}$	Rate of delignifi- cation $= 1/t_{90\%}$
A	75	0.16	1.54	1.38	2.35	116	13.28	0.075
	72	0.18	3.50	3.32	2.03	586	4.74	0.211
	71	0.18	4 89	4.71	1.94	414	3.41	0.293
	73	0.17	6.75	6.58	1.86	600	2.48	0.403
B	60	0.39	2.18	1.79	2.53	164	7 26	0 138
	59	0.41	3.69	3.28	2.30	318	4.23	0.237
	63	0.40	5.19	4.79	2.21	466	3.04	0.329
	62	0.40	6.94	6.54	2 12	642	2.26	0.443
	74	0.41	9.26	8.85	2.00	878	1.75	0.572
	66	0.42	12.06	11.64	—	1164	1.40	0.715
C	56*	0.87	2.40	1.53	2.80	178	6.68	0.150
	51	0.91	3.23	2.32	2.66	262	5.08	0.197
	77	0.92	3.95	3.03	2.56	330	3.94	0.254
	76	0.91	4.97	4.06	2.46	425	3.04	0.329
	52	0.93	5.04	4.11	2.45	434	3.07	0.326
	53	0.91	7.14	6.23	2.29	628	2.28	0.438
	55	0.87	9.78	8.91	2.16	875	1.78	0.562
	61	0.92	13.00	12.08	—	1185	1.37	0.730
D	67	1.44	6.24	4.80	—	—	2.31	0.433
	68	1.38	9.33	7.95	—	—	1.77	0.565
	69	1.39	12.65	11.26	—	—	1.43	0.700

Precipitation of calcium sulphite occurred.

The rate of delignification is plotted against the free sulphur dioxide in Fig. 5, and against the excess sulphur dioxide in Fig. 6 for the different series of combined sulphur dioxide. Runs Nos. 64, 65, and 67 are omitted because of the uncertainty introduced by precipitation of calcium sulphite. From these curves it is quite clear that the free sulphur dioxide gives the best relation, since there is no variation with the combined except at high concentrations. This will be explained later. Furthermore, if the curve is extrapolated to zero concentration, it is seen that the rate becomes zero for zero free sulphur dioxide.
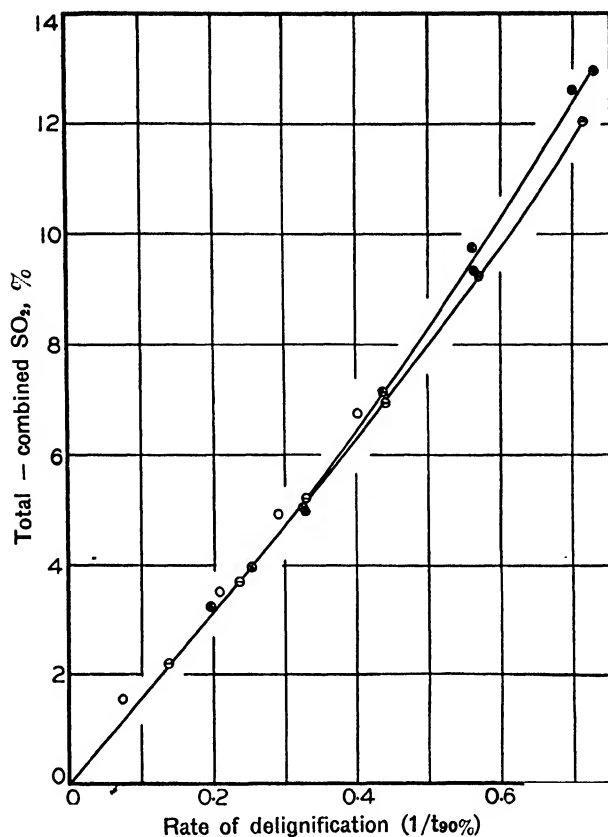
FIG. 5.   *The rate of delignification of spruce wood at 130° C. as a function of the free sulphur dioxide.*

Series	○ A	⊖ B	⊗ C	● D
Combined SO₂, %	0.2	0.4	0.9	1.4

In Fig. 6, on the other hand, the four series of combined sulphur dioxide give distinctly separate curves which cannot be extrapolated to zero rate at zero concentration of excess sulphur dioxide. This proves that the excess sulphur dioxide of Miller *et al.* is not the controlling factor in determining the rate of delignification. If the rate is plotted against the total — $1.5 \times$ combined, as suggested by the results of Gishler and Maass (5), a relation is obtained midway between those illustrated in Figs. 5 and 6. No support can be given to such a relation from the evidence of actual cooking obtained here. The ordinary free sulphur dioxide gives the best measure of the rate of cooking, independently of the combined. However, low concentrations of combined sulphur dioxide are possible only at high liquor ratios, since a definite quantity of lime equal to about 5% of the weight of the wood is necessary to neutralize the lignosulphonic acids produced.
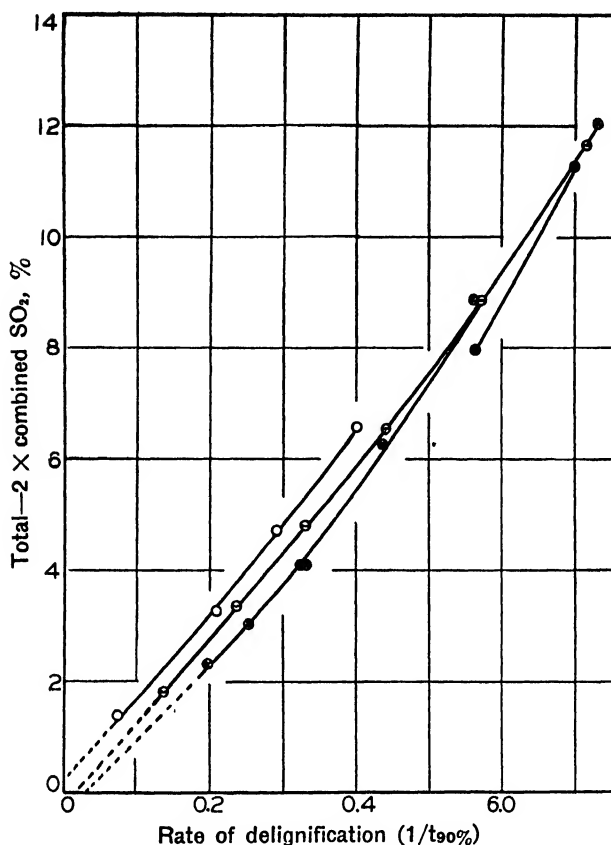
FIG. 6.   *The rate of delignification of spruce wood at 130° C. as a function of the "excess"*
sulphur dioxide.

Series	O A	⊖ B	⊗ C	● D
Combined SO₂, %	0.2	0.4	0.9	1.4

The Relation of the Partial Pressure of Sulphur Dioxide to the Rate of
Delignification

Since the free sulphur dioxide was found to be the controlling factor in
determining the rate of delignification, further calculations were of interest.
The sulphur dioxide in solution that is not in combination with the lime is
proportional to the partial pressure of the gas, and since the equilibrium
relations between the different ionic and molecular species are so complex,
the partial pressure of sulphur dioxide is a better measure of the true free
sulphur dioxide than the value calculated from the difference between the
total and the combined.

The most accurate measurements of the vapor pressure of sulphite liquor
for various concentrations and temperatures have been carried out in this
laboratory by Beazley (1).   The partial pressure of sulphur dioxide at 130° C.

was obtained for each liquor concentration where data were available.   It was necessary to extrapolate to obtain the vapor pressures at concentrations greater than 6% sulphur dioxide, but since the relation is linear except at low concentrations, the extrapolated values are considered accurate.

These partial pressures are given in Table III and are plotted against the rate of cooking in Fig. 7.   It is seen that all the points fall on the same curve, irrespective of the combined sulphur dioxide, and that the relation is much more uniform than that given by the calculated free sulphur dioxide in Fig. 5. It is also noticed that Fig. 7 shows a very definite curvature, greater than any experimental error, such that the rate of cooking increases less rapidly at the higher partial pressures.
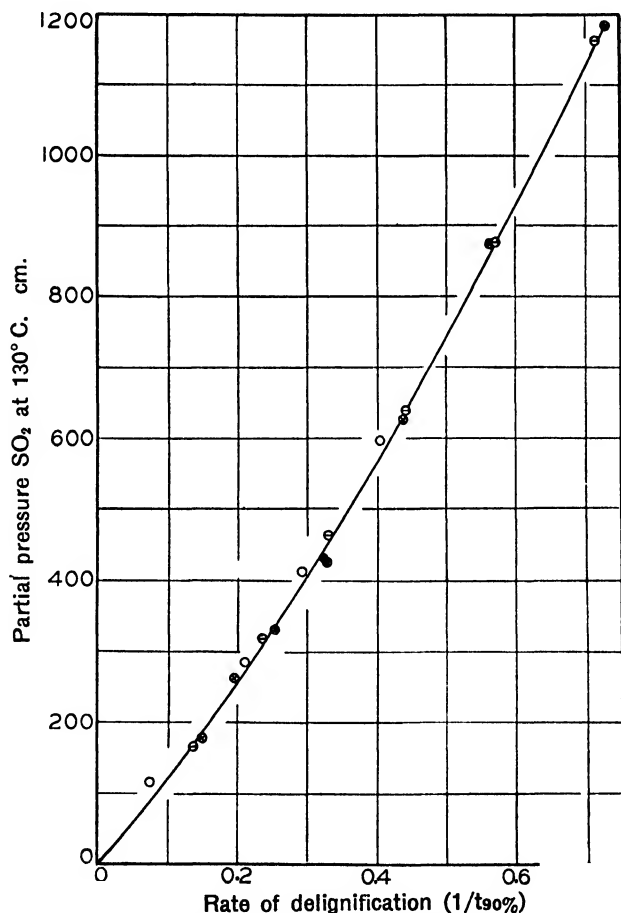
FIG. 7.   *The rate of delignification of spruce wood at 130° C. as a function of the partial pressure of sulphur dioxide.*

Series	O A	⊖ B	⊗ C
Combined SO₂, %	0.2	0.4	0.9

A consideration of the equilibria existing in sulphite liquor is necessary before any further explanation is offered. From a study of the system, calcium-oxide–sulphur-dioxide–water, Gishler and Maass (5) have shown that the following relations hold:

$$P = K_1(SO_2) \tag{4}$$

where P is the partial pressure of sulphur dioxide gas; and

$$(SO_2)(H_2O) = K_2(H_2SO_3) \tag{5}$$

$$(H_2SO_3)K_3 = (H^+)(HSO_3^-) \tag{6}$$

from which it follows that

$$P = \frac{K_1K_2(H_2SO_3)}{(H_2O)} = \frac{K_1K_2(H^+)(HSO_3^-)}{K_3(H_2O)} . \tag{7}$$

Equation (7) shows that, provided that the concentration of water is considered constant, the partial pressure of sulphur dioxide is proportional to the concentration of sulphurous acid or the product of the concentration of the hydrogen and bisulphite ions. This relation is quite independent of the presence of lime. The addition of calcium monosulphite to the cooking liquor does not affect the rate of delignification, since the rate is independent of the combined sulphur dioxide, when the free is constant. The decrease in hydrogen ion concentration must be compensated for by the increase in bisulphite ion concentration.

Apart from considerations of the mechanism of the reaction, this suggests that the active cooking agent in sulphite liquor is either sulphurous acid or the hydrogen and bisulphite ions together, and not either ion separately, as has been frequently claimed. This agrees with a statement of Miller *et al.* (14), that the removal of lignin is the result of the specific action of ionized sulphurous acid, but that the effective cooking action could not be attributed to the bisulphite ion alone.

Gishler and Maass (6) have shown that the bisulphite ion in sulphite liquor is strongly buffered and increases only slightly with the concentration of free sulphur dioxide. Increase in the combined, however, causes a large increase in bisulphite. Hence according to Equation (7), an increase in the hydrogen ion concentration by the addition of sulphur dioxide, or an increase in bisulphite ion concentration by the addition of both lime and sulphur dioxide, will increase the partial pressure of the gas as well as the rate of delignification. This explains the relation in Fig. 7.

There are three possible explanations for the curvature observed in Fig. 7:

(a) At the high sulphur dioxide concentrations, cooking is so rapid that diffusion of the lime into the wood-meal may not be fast enough to prevent a local high acidity which might cause slight burning and thus hinder cooking. Some evidence for this was found in a few cases, in which a slight discoloration of the wood-meal was observed at the bottom of the bomb. On the other hand, the relation appears to be much too uniform to be attributed to such

an uncertain cause, and is substantiated qualitatively by the results of McGovern (13), already mentioned.

(b) A second possible explanation may be found by rewriting Equation (7):

$$P(H_2O) = K(H_2SO_3) = K'(H^+)(HSO_3^-) \tag{8}$$

Since the liquors are concentrated, it is not permissible to assume that the concentration of water is constant, as is assumed in the case of dilute solutions. If the cooking action is due to sulphurous acid or the hydrogen and bisulphite ions together, Equation (8) shows that a linear relation with the rate would be obtained only by multiplying the partial pressure of sulphur dioxide by the molar concentration of water. Since this factor is smaller at higher concentrations of liquor, it would tend to straighten the curve in Fig. 7.

An attempt to verify this was made by calculating the concentration of water. No data were available on the density of sulphite liquor in the concentration and temperature range desired. Therefore, the density of sulphurous acid solutions reported by Campbell and Maass (2) was extrapolated to 130° C., and this value used as the closest approximation. It was found that the relation obtained by taking into account the water concentration was slightly closer to the linear than that shown in Fig. 7. However, there was still a curvature greater than the experimental error. It is possible that hydration of the ions present, which would lower the (H2O) still further, might account for the deviation from the linear relation. This would be impossible to calculate.

(c) A third explanation may be found in Fig. 8, in which the logarithm of the partial pressure of sulphur dioxide is plotted against the logarithm of the rate of delignification. It is observed that an excellent straight line is obtained. This follows the equation of the Freundlich adsorption isotherm and suggests the possibility of an adsorption process. The colloidal nature of lignin has frequently been stressed, and if the concentration of the active cooking agent at the surface of the lignin particles was greater than in the body of the solution, such a relation would hold. That this relation has been found, does not, of course, prove that an adsorption process is involved, but the agreement seems too close to be entirely fortuitous.

The Relation of Hydrogen Ion Concentration to the Rate of Delignification

More information may be obtained from a study of the hydrogen ion concentration of the cooking liquors. It is realized that the presence of the wood may alter the pH slightly, owing to the formation of lignosulphonic acids. However, the very high liquor ratio used will minimize any such change during cooking, so that interpretation of the data is possible.

The actual hydrogen ion concentration of sulphite liquor at cooking temperatures cannot be measured directly. Gishler and Maass (5) have made calculations up to 90° C. from vapor pressure and conductivity measurements. The logarithm of the hydrogen ion concentration plotted against the reciprocal of the absolute temperature gives a straight line. This makes accurate extra-
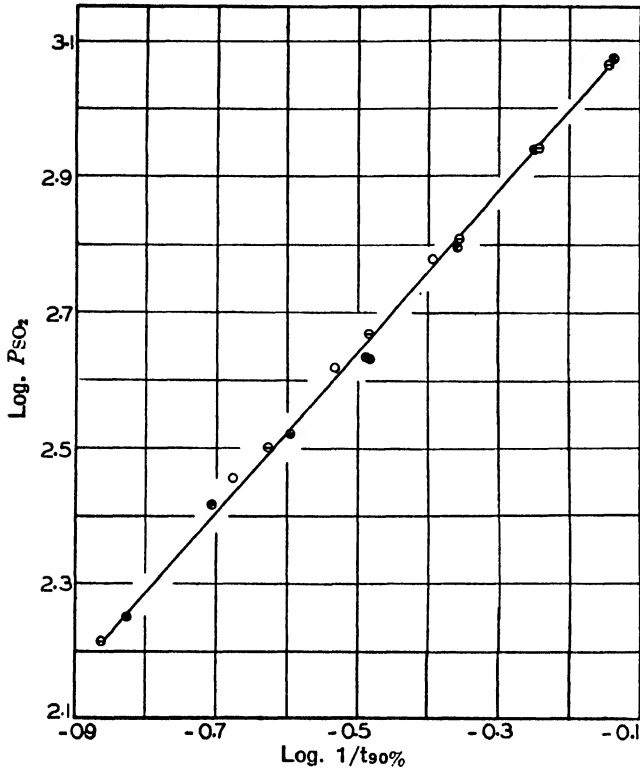
FIG. 8.   The *rate of delignification of spruce wood at 130° C. as a function of the partial pressure of sulphur dioxide.*

Series	O A	⊖ B	⊗ C
Combined SO₂, %	0.2	0.4	0.9

FIG. 9.   The rate of delignification of spruce wood at 130° C. as a function of the hydrogen ion concentration of the liquor.

Series	A	B	C
Combined SO₂, %	0.2	0.4	0 9

polation to 130° C. possible.   A less accurate extrapolation for concentrations above 6% sulphur dioxide was necessary.   In this way the actual pH of each liquor was calculated, where possible, and is given in Table III.

In Fig. 9 the logarithm of the rate of delignification is plotted against the pH of the liquor at 130° C. for three series of combined sulphur dioxide. It is observed that a straight line relation is obtained and that the three series give three distinctly separate lines of almost the same slope.   The time required for the amount of delignification to increase from 80 to 90% and from 90 to 95% was also calculated.   The logarithms of the reciprocals of these times were plotted against the pH of the liquor; this gave relations similar to those of Fig. 9.   Here again, three concentrations of combined sulphur dioxide gave three well separated curves.   This leads to some rather interesting deductions.   Obviously, the rate of cooking cannot be governed by the hydrogen ion concentration alone, or all the points would be on a single line.   Evidently the addition of both lime and sulphur dioxide in such proportions that the hydrogen ion concentration is not altered will greatly increase the rate of lignin removal.

This can be explained only on the basis of the theory already outlined, that the cooking action is due to sulphurous acid or the hydrogen and bisulphite ions together, and not to either ion separately.   The addition of lime, together with sufficient sulphur dioxide to keep the hydrogen ion concentration constant, increases the bisulphite ion concentration, and hence the rate of cooking.   If the combined is held constant, an increase in the free sulphur dioxide increases the hydrogen ion concentration (lowers the pH, Fig. 9), and again increases the rate of cooking.

Discussion

Various theories regarding the mechanism of the delignification of wood in the sulphite process have been proposed.   Hägglund (8, 10) considers the reaction as taking part in two stages, *viz.*, first, a sulphonation of the lignin in the solid phase by an addition to some unsaturated linkage in the lignin molecule, and second, an hydrolysis of the sulphonated lignin which separates it from the wood.   The rate of the first reaction is supposedly determined by the bisulphite ion concentration and is rapid in comparison with the second.   The hydrolysis reaction should then govern the over-all rate of cooking, and would be determined by the hydrogen ion concentration of the liquor.

In support of this theory, Hägglund (9) showed that partially sulphonated wood could be cooked in buffer solutions at a rate that increased with the hydrogen ion concentration of the buffer.   Yorston (21) made similar two stage cooks, and found that the rate of removal of lignin in the buffer solution depended on the initial sulphur content of the lignin, as well as on the hydrogen ion concentration of the buffer.   Interpretation of the results was complicated by the fact that sulphonation of the lignin was not uniform.   However, he

concluded that once the lignin contained a minimum of 6% sulphur, the rate of subsequent cooking was governed by the hydrogen ion concentration of the liquor.

The present investigation does not substantiate the above conclusion.   It is difficult to explain the results on the basis of Hägglund's theory, since the authors have shown that the hydrogen ion concentration alone is not the controlling factor in determining the rate of cooking.   Yorston (19, 20), from a measurement of the degree of sulphonation at various stages in cooking, concluded that the sulphonation reaction was slow enough to limit to some extent the rate of pulping.   He also found that more sulphur was combined with the lignin than was necessary for subsequent cooking in a buffer solution. It is therefore suggested that the sulphonation reaction governs the rate of cooking and is determined by the product of the concentrations of the hydrogen and bisulphite ions, and not by either ion alone.   If sulphonation is stopped by replacing the liquor by a buffer solution, naturally the subsequent cooking will be determined by the hydrogen ion concentration of the buffer.

The results reported above indicate the failure of existing theories to explain all the observed facts in regard to sulphite cooking.   Possible interpretations have been made, but much more information is needed before the mechanism of the reaction can be completely elucidated.   From a practical point of view, a considerable number of data have been provided for a study of sulphite cooking under conditions approaching commercial practice.   The effect of various constituents of the liquor on the yield of pulp has been clearly shown, so that the most advantageous conditions may be chosen.

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PASTURE STUDIES XII

₁ THE NATURE OF THE ORGANIC PHOSPHORUS IN SOILS[1]

By C. L. Wrenshall[2] and R. R. McKibbin[3]

Abstract

An improved procedure for the separation of nucleic acid material from soil is described. By its use as much as 65% of the apparent organic phosphorus in soil has been separated in the nucleic acid fraction; this shows that most of the soil organic phosphorus exists in this form. Material of this nature enters the soil solution.

The material separated yielded, on hydrolysis, phosphoric acid, pentose sugar, adenine, and uracil. This indicates that it is a mixture of mononucleotides.

The presence of traces of ether-soluble phosphorus in soil was confirmed.

The presence of organic phosphorus compounds in soil has been established by the finding of ether-soluble phosphorus in low concentration by Aso (1) and by Stoklasa (20), and by the isolation of phosphorus-bearing material of a nucleic acid nature by Shorey (18) and by Bottomley (4). Methods for estimating the organic phosphorus content of soil have been proposed by Potter and Benton (12) and by Schollenberger (16). Analyses made according to these methods, and by other means, have revealed that soils, in general, contain considerable amounts of organic phosphorus compounds (2, 6, 9, 17).

Shorey and Bottomley did not record the yield of phosphatic material obtained, nor its phosphorus content, so that the proportion of the total phosphorus contained therein cannot be calculated from their data. Shorey intimated that his method of isolation was inefficient to the extent that no estimate of the total amount of nucleic acid could be made. Schmoeger (15) and Aso (1) believed that the greater part of the organic phosphorus of soil was of nuclein nature. Schollenberger (16) and Auten (3) failed, however, to obtain evidence of the presence of any considerable quantity of nucleic acid.

To define the organic phosphorus of soils, it is necessary to determine the amounts present in the forms already detected, namely, lecithin and nucleic acid, and to establish the identity and abundance of other organic compounds of phosphorus should such be present in soil. This paper is mainly concerned with the first of these considerations.

Experimental Methods

The method of Potter and Benton (12) was used to estimate the total organic phosphorus in soil. Organic phosphorus in solution was estimated by the method of Parker and Fudge (10). These methods were considered to be sufficiently accurate for the purpose of this study.

Lipoid phosphorus was estimated by exhaustively extracting a sample of soil first with ether and then with absolute ethanol, and determining the total ether-soluble phosphorus in the extracts.

The separation of nucleic acid was effected by a procedure similar in principle to that used by Shorey (18) but modified in the following respects: The soil under study was first extracted with dilute acid so that a maximum amount of phosphorus would then be dissolved by dilute alkali (16, 19). Ammonium hydroxide was used instead of sodium hydroxide for dissolving the organic matter, as the excess could be removed without neutralization. The "humic acid" was reprecipitated to recover the nucleic acid carried down in this fraction (13). A higher concentration of alcohol was necessary to obtain complete precipitation of the nucleic acid. The duration of the treatment was made as short as possible, and care exercised at all stages to minimize hydrolytic destruction. The details of the procedure employed are as follows:

A suitable quantity of soil (100 to 1000 gm.) was extracted with cold N hydrochloric acid until the leachings were virtually free from calcium. The soil was washed with distilled water until practically free from acid, and then extracted for 24 hr. by occasional agitation with 10 times its weight of cold 4% ammonium hydroxide. The dark liquor was siphoned from the settled soil to a vacuum distillation apparatus, and the excess ammonia removed by volatilization at a temperature below 40° C. The almost neutral liquid was acidified with $2N$ hydrochloric acid, and the precipitate of "humic acid" allowed to settle. The supernatant liquid was decanted through a free-flowing filter paper, and finally the precipitate was transferred to the filter and washed once with distilled water.

The precipitate was redispersed in the minimum amount of 4% ammonium hydroxide, and the volume was made up with water to that of the original alkaline extract. The excess of ammonia should be slight. After acidifying, decanting, and filtering as before, the acid filtrates were combined. The reprecipitation of the "humic acid" was repeated a second time. In general, further reprecipitation did not lead to an increase in the yield of organic phosphorus.

The acid filtrates were neutralized as obtained, and any precipitate that formed was discarded. The combined filtrates were concentrated by vacuum distillation below 35° C. until further distillation was difficult. The concentrate was acidified with 5% of its volume of concentrated hydrochloric acid, and introduced with vigorous stirring into five times its volume of commercial absolute ethanol. A finely divided, gelatinous precipitate formed immediately, slowly coalesced, and sank to the bottom after several hours. The supernatant liquid was decanted and the precipitate collected on a hardened filter paper, with gentle suction. It was washed with acidified 95% ethanol, and finally with absolute ethanol. The filtrate was free from organic phosphorus, and the precipitate was free from inorganic phosphate. After complete drying in a vacuum desiccator the product was a light-brown amorphous substance that crumbled readily to a powder.

The organic phosphorus-bearing material was examined by the methods outlined by Jones (5) in order to establish its nucleic acid character.

Experimental Data

A sample of typical black muck soil, containing 0.212% of phosphorus in the air-dried state, was examined. The Potter and Benton method of analysis indicated that 55.4% of the total phosphorus was organically combined. Of the total organic phosphorus, 0.31% was shown to be ether-soluble, and 65.0% was present in the nucleic acid precipitate. The latter figure was obtained from the following data: 100 gm. of the soil was extracted with 1200 cc. of 4% ammonium hydroxide, of which one litre was decanted. Following the procedure already described, a yield of 1.12 gm. of impure nucleic acid material was obtained. This material was free from inorganic phosphate but contained 5.67%, or 0.0635 gm., of phosphorus in organic combination. According to the Potter and Benton analysis, 0.0995 gm. of organic phosphorus should have been present in the litre of alkaline extract. On this basis the recovery of organic phosphorus in the nucleic acid precipitate was 65.0%.

A sample of typical brown forest soil (8) contained 0.071% of phosphorus of which 31.2%, according to the Potter and Benton method, was in organic combination. Of the total organic phosphorus 0.25% was shown to be ether-soluble, and 47.5% was present in the nucleic acid precipitate.

The observation of Pierre and Parker (11) that organic phosphorus is a normal constituent of soil water is substantially confirmed here. Table I shows the relative amounts of organic and inorganic phosphorus appearing in water extracts of pasture soils of the brown forest soil type.

TABLE I

PHOSPHORUS IN WATER EXTRACTS OF SOIL

Sample designation	Concentration of phosphorus, parts per million of solution		
	Total	Inorganic	Organic
R—untreated	0.225	0.047	0.178
R—fertilized with superphosphate	0.365	0.204	0.161
D—untreated	0.160	0.011	0.149

In other work carried on in this laboratory (14), large quantities of water percolate from podsol raw humus had been concentrated *in vacuo*, and the material insoluble in 70% ethanol separated and dried. Ten grams of this material was dispersed in 200 cc. of 5% hydrochloric acid and poured into one litre of absolute ethanol in the manner described for the separation of nucleic acids. A precipitate formed; it was separated in the usual way. The dry product weighed 0.76 gm. and contained 3.63% of phosphorus in organic combination.

A composite sample of the organic phosphorus-bearing material obtained in a number of experiments was shown to yield, on hydrolysis, the following:

(a) Pentose sugar; demonstrated by evolution of furfural, by positive reactions with phloroglucin and orcin, and by reduction of Fehling's solution.

(b) Phosphoric acid; precipitable as magnesium-ammonium-phosphate or ammonium-phospho-molybdate.

(c) Adenine; isolated as the picrate, clusters of pale yellow needles melting at 271° C.* with decomposition.

(d) Uracil; isolated as colorless needle clusters melting with decomposition at 330° C. after first turning brown at 280° C. This substance would not form a picrate, and responded to the Wheeler and Johnson color reaction for pyrimidines.

No other purine or pyrimidine substances could be demonstrated in the hydrolysate.

Discussion

The hydrolytic products of the organic phosphorus-bearing material separated from soil show its nucleic acid character, and the claims of previous workers in this respect are thus substantiated. The constituents reported here are the same as those obtained by Bottomley (4) on decomposing similar material extracted from English peat. Bottomley concluded that the material was adenine-uracil dinucleotide. However, this conclusion is probably incorrect. Levene and co-workers (7) have demonstrated that the adenine-uracil dinucleotide supposed to result from a decomposition of plant nucleic acids is, in reality, a mixture of two mononucleotides separable by fractional crystallization. Thus the factual existence of an adenine-uracil dinucleotide has never been demonstrated, and its occurrence is held to be most unlikely. The components of the material isolated by Shorey (18) were not the same as those reported here, and varied from soil to soil. In no case have all the components of nucleic acid been detected together in one of these preparations —guanine has never been reported—so that it is most unlikely that unchanged nucleic acid persists to an appreciable extent in soil. Altogether it seems most logical to conclude that the material separated from soil is a mixture of mononucleotides, in the present instance a mixture of adenine nucleotide (adenylic acid) and uracil nucleotide (uridylic acid).

As the figures for the phosphorus content indicate, the material obtained in this study was far from pure. On ignition, a large ash containing some iron remained. Reprecipitation did not result in a pure product, as the phosphorus content was not enhanced, nor were the characteristics of the material improved. In so far as can be judged from their descriptions, the previous preparations of a similar nature were likewise very impure.

*Melting points are uncorrected.

The data for the percentage yield of organic phosphorus obtained in the ether-soluble and nucleotide fractions indicate that ether-soluble phosphorus is present in very low concentration, while the nucleotide phosphorus is the most abundant form of organic phosphorus present in soil. Additional force is given to the latter statement by the crudeness of the means of estimating the nucleotide phosphorus; unquestionably some of this material was destroyed and lost in the course of separation. The amounts actually present in the soils must be materially greater than those reported. It may very well be that nucleotides are the only organic phosphorus compounds which persist in soil to any considerable extent.

The presence of appreciable quantities of organic phosphorus in water extracts of soils, and the separation of nucleotide phosphorus from a water extract of podsol raw humus, indicate that nucleotides are normal constituents of the soil solution.

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A SYNTHESIS OF 1-HYDROXY-2-NAPHTHOIC NITRILE[1]

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Abstract

The neutral product of the condensation of phenylacetaldehyde with ethyl *sodio*cyanoacetate when distilled under low pressures loses the elements of ethyl alcohol and forms 1-hydroxy-2-naphthoic nitrile. This is identical with the synthetic substance prepared through a series of reactions from α-naphthol. The methyl ether has been prepared from both the synthetic substance and the product of the condensation. 1-Hydroxy-2-naphthoic nitrile can be coupled readily with *p*-nitrobenzenediazonium chloride. The evidence relating to the structure of the neutral condensation product is reviewed.

The condensation of phenylacetaldehyde with ethyl cyanoacetate has been investigated by Haworth (3) and later by Linstead and Williams (7). According to the former the reaction produces mainly ethyl α-cyano-α-styrylacetate (II),
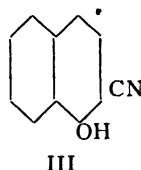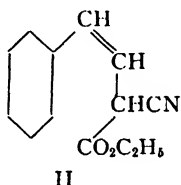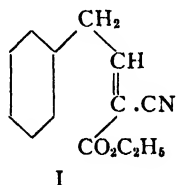
together with αα'-dicyano-β-benzylglutaric acid. On the other hand, Linstead and Williams hold that the product consists of a mixture of (II) and ethyl α-cyano-β-benzylacrylate (I) in which the form (II) predominates. These authors make no mention of the substituted glutaric acid, possibly because in most of their work diethylamine was used as the condensing agent instead of the sodium ethoxide used by Haworth.

In the course of a reinvestigation of this reaction it has been found, as already known, that the product consists principally of an ester fraction together with αα'-dicyano-β-benzylglutaric acid. With the exception of the melting point, the properties of this acid have been found to agree with those recorded by Haworth; he gives the melting point as 173° C. while the authors were unable after many recrystallizations to raise the melting point beyond 168° C*. Therefore, it was identified further by conversion to β-benzylglutaric acid.

αα'-Dicyano-β-benzylglutaric acid is obtained also when phenylacetaldehyde is shaken with aqueous sodium cyanoacetate. It is then accompanied by two other acidic fractions which can be separated through their barium salts. It was thought that these two fractions might be chiefly the acids corresponding to esters (I) and (II), but it was not found possible to obtain them sufficiently pure for identification.

* *All melting points determined by us are corrected.*

The ester fraction can be distilled at 182° C. at 15 mm., but at pressures of 2 to 4 mm. distillation is accompanied by a great deal of frothing, and a crystalline substance is deposited in the condenser. This substance, after recrystallization from benzene, melts at 178° C. It is phenolic in character but otherwise neutral and can be sublimed unchanged at 145° to 150° C. at 1 mm. Its analytical figures are in excellent agreement with $C_{11}H_7ON$, although the molecular weight determined by the Rast method is high (204; calcd. 169). It may be pertinent to mention here that this substance is not identical with that compound (m.p. 220° C.), which Linstead and William, isolated in a condensation catalyzed by sodium ethoxide. In one of our condensations which seemed to behave abnormally, a compound (m.p. 226° C.), apparently identical with that isolated by Linstead and Williams, separated from the ethereal solution of the product during treatment with dilute sodium bicarbonate, but was obtained in amount insufficient for further examination.

The composition of the distillation product, m.p. 178° C., differs by C_2H_6O from that of ester (I) or (II), which, therefore, seems to have been derived from it by loss of ethyl alcohol accompanied by ring closure, and it appears certain that the transformation must have taken place during the heating under low pressure. For this compound the most probable structure appeared to be that of 1-hydroxy-2-naphthoic nitrile (III). Both structures (I) and (II) lend themselves to such ring closure involving simultaneous hydrogen wandering, although it would seem that the transformation might proceed more readily from the $\beta\gamma$-form (II).

Such a reaction is not unique but comparable with the well known synthesis of α-naphthol from β-benzylidene-propionic acid (1). Recently Menon (9) found a strictly analogous case in the production of ethyl 1-hydroxy-naphthalene-2, 4-dicarboxylate instead of the expected ethyl γ-carbethoxy-α-phenylglutaconate from the condensation of ethyl phenylacetate and ethyl ethoxymethylmalonate in the presence of sodium ethoxide. Menon (10) has observed lately several other examples using halogenated phenylacetic esters and naphthylacetic ester in place of ethyl phenylacetate. It is noteworthy that in the production of ethyl 1-hydroxynaphthalene-2, 4-dicarboxylate, as in that of 1-hydroxy-2-naphthoic nitrile now placed on record, ring closure takes place during distillation *in vacuo*.

For the complete identification of this reaction product the synthesis of 1-hydroxy-2-naphthoic nitrile was effected. α-Naphthol was converted by the Kolbe reaction into 1-hydroxy-2-naphthoic acid. This on reduction gave rise to 1-hydroxy-2-naphthaldehyde. The oxime of this aldehyde when treated according to Passerini's method (11) was converted smoothly into 1-hydroxy-2-naphthoic nitrile, m.p. 179° C. This melting point was not depressed when this substance was admixed with the condensation product, m.p. 178°C. The methyl ethers prepared from the two substances had the same melting point (50° to 51° C.) either alone or after admixture. An attempt to prepare the benzoates, however, led to abnormal

products which, although identical with each other, did not agree in composition with that of the expected benzoate. 1-Hydroxy-2-naphthoic nitrile couples readily with *p*-nitrobenzenediazonium chloride, giving rise to a highly colored product, m.p. 275° C., presumably, 4-*p*-nitrobenzeneazo-1-hydroxy-2-naphthoic nitrile.

Herz and Schulte (4) prepared this nitrile from 2-cyano-1-naphthalene-sulphonic acid (m.p. 179° C.). Passerini and Grulis (12) also obtained it as a product of the reaction of mercury fulminate on an alcoholic solution of α-naphthol and potassium cyanide. The melting point given by them (171° to 172° C.) shows, however, that their product was not quite pure.

It seems doubtful if Linstead and Williams have adduced sufficient evidence to warrant their conclusion, which has been accepted by Hugh and Kon (5) that the ester derived from condensing phenylacetaldehyde with ethyl cyanoacetate consists mostly of the βγ-form (II) in equilibrium with some of the αβ-form (I). Aside from the physical evidence of the exaltation of the molecular refractivity, which Linstead and Williams consider is untrustworthy in the present instance, there is little if any chemical evidence to support the βγ-structure. The authors have found that the ester fraction, b.p. 182° C. at 15 mm., reacted readily with potassium cyanide to add on the elements of hydrogen cyanide, and that the product on hydrolysis gave rise to benzylsuccinic acid. This, and the ready reaction with ethyl cyanoacetate and ammonia investigated by Linstead and Williams, support the αβ-structure. The great reluctance of the substance to add ozone, observed by Linstead and Williams, which the authors confirm fully, also supports the αβ-unsaturated formula. In a similar instance it has been shown previously (8) that while the αβ-unsaturated ethyl cyclohexylidene-cyanoacetate reacts very slowly with ozone, ethyl α-*n*-butyl-Δ'-cyclohexenylcyanoacetate and the corresponding ethyl α-*n*-ethyl-Δ'-cyclohexenylcyanoacetate, both of which having the double bond undoubtedly in the βγ-position, react rapidly (2). The production of αα'-dicyano-β-benzylglutaric acid in the reaction itself is likewise indicative of the αβ-phase. The evidence on which Linstead and Williams rely chiefly is the oxidation of the ester to benzoic acid by a solution of chromic acid in acetic acid. They state that under the conditions used by them phenylacetaldehyde is not oxidized to benzoic acid. Repeated efforts have been made to confirm this statement, but in every experiment that the authors performed, following as exactly as possible the conditions used by Linstead and Williams, benzoic acid was obtained as an oxidation product of phenylacetaldehyde.

Thus it may be concluded that the evidence for the predominance of Structure (II) in the product of the condensation of phenylacetaldehyde with ethyl cyanoacetate is little if any stronger than that adduced for maintaining that the product of the condensation of cyclohexanone with ethyl cyanoacetate is ethyl cyclohexenylcyanoacetate (2), rather than the ethyl cyclohexylidene-cyanoacetate (6) which it is now generally accepted to be.

Experimental

Condensation of Phenylacetaldehyde with Ethyl Cyanoacetate

A mixture of 12 gm. of phenylacetaldehyde with ethyl *sodio*cyanoacetate prepared from 11.5 gm. of ethyl cyanoacetate and 2.3 gm. of sodium dissolved in 45 cc. of absolute alcohol was refluxed on the steam bath. The product was separated into an acid and a neutral fraction. The acid fraction yielded $\alpha\alpha'$-dicyano-β-benzylglutaric acid which, recrystallized from chloroform-petroleum ether mixture, melts at 168° C. Calcd. for $C_{14}H_{12}O_4N_2$: N, 10.6%: equiv. 272. Found: N, 10.3%; equiv. 273. On hydrolysis this acid gave rise to β-benzyl-glutaric acid, m.p. 101° C. Calcd. for $C_{12}H_{14}O_4$: equiv. 222. Found: equiv. 222.4. The ester distilled at 182° C. at 15 mm. but when distilled under 2 to 4 mm. frothed a great deal, and eventually yielded a small quantity of oil and the crystalline 1-hydroxy-2-naphthoic nitrile which was recrystallized from methanol-benzene, m.p. 178° C. Calcd. for $C_{11}H_7ON$: C, 78.10; H, 4.14; N, 8.28%. Found: C, 77.87, 78.03; H, 4.33, 4.23; N, 8.31, 8.46%.

Formation of Benzylsuccinic Acid from the Ester

To 8 gm. of the ester dissolved in 80 cc. of alcohol was added 5 gm. of potassium cyanide dissolved in 7 cc. of water. After standing two weeks in a dark place the product was hydrolyzed at 0° C. with fuming hydrochloric acid, and it yielded 2.8 gm. of benzylsuccinic acid obtained from hot water as glistening plates, m.p. 162° C. Calcd. for $C_{11}H_{12}O_4$: C, 63.46; H, 5.77%; equiv. 208. Found: C, 63.30; H, 5.74%; equiv. 210.

Synthesis of 1-Hydroxy-2-naphthoic Nitrile

1-Naphthol-2-carboxylic acid was prepared by Kolbe's reaction by leading a strong current of carbon dioxide for eight hours into a mixture of α-naphthol and sodium in boiling toluene. The purified acid, m.p. 203° C., was reduced with sodium amalgam to the corresponding aldehyde which was immediately converted into the oxime, m.p. 145° C. (Yield 43%, based on acid used, deduction being made of the recovered acid.) The oxime was then converted into the nitrile by Passerini's reaction (11) as follows: 4 gm. of 1-hydroxy-2-naphthaldoxime and 1.8 gm. of powdered potassium cyanide were dissolved in 14 cc. of alcohol and 4.8 cc. of water, and the solution was refluxed on the steam bath for five hours. The alcohol was then evaporated, water added, and the solution filtered through charcoal. The filtrate was acidified with dilute sulphuric acid and the precipitated nitrile filtered, washed with water, dried, and sublimed at 160° to 170° C. at 0.5 to 1 mm. It was recrystallized (charcoal) from methanol-benzene; prisms, m.p. 179° C., wt. 2.1 gm. Yield, 58.3%. Calcd. for $C_{11}H_7ON$: C, 78.10; H, 4.14; N, 8.28%. Found: C, 78.29, 78.30; H, 4.38, 4.46; N, 8.24, 8.50%.

Methylation of 1-Hydroxy-2-naphthoic Nitrile

Some of the nitrile obtained from the condensation product (0.05 gm.) was dissolved in ether (20 cc.) containing 1 cc. of methanol, and treated at room temperature for 16 hr. with an ethereal solution of diazomethane. The excess

reagent was evaporated and the product in ether solution was washed with dilute sodium hydroxide, dried, and eventually crystallized from benzene-petroleum ether; long needles, m.p. 50° to 51° C. Calcd. for $C_{12}H_9ON$: OCH_3, 16.94%. Found: OCH_3, 16.98%. The methyl ether was also prepared in the same way from the synthetic product, m.p. 49° C. Found: OCH_3, 16.73%. Admixture of the two methylated nitriles did not depress the melting point (m.p. 50° to 51° C.).

Benzoylation of 1-Hydroxy-2-naphthoic Nitrile

This reaction followed an anomalous course. 1-Hydroxy-2-naphthoic nitrile (from condensation), 0.1 gm., was dissolved in 3 cc. of pyridine, and the solution was warmed on the steam bath for one hour with 0.7 cc. of benzoyl chloride, and then allowed to stand at room temperature for some time. The product was worked up in the usual way and crystallized (charcoal) from benzene, m.p. 159° to 160° C. Calcd. for $C_{18}H_{11}O_2N$: N, 5.13%. Found: N, 7.21, 7.34%. The synthetic nitrile was also treated with benzoyl chloride in pyridine in the same way, m.p. 159° to 160° C. Found: N, 7.16, 7.15%. Admixture of the two products of benzoylation did not depress the melting point; the two, therefore, appear to be identical but do not agree in composition with the expected benzoate.

4-p-Nitrobenzeneazo-1-hydroxy-2-naphthoic Nitrile

1-Hydroxy-2-naphthoic nitrile (0.5 gm.) was dissolved in potassium hydroxide solution and coupled with p-nitrobenzenediazonium chloride prepared from p-nitraniline (0.3 gm.), sodium nitrite (0.2 gm.), and 1.5 cc. of hydrochloric acid. The azo compound was crystallized from nitrobenzene from which it separated as reddish flakes with a greenish cast, m.p. 275° C. Calcd. for $C_{17}H_{10}O_3N_4$: C, 64.15; H, 3.14; N, 17.61%. Found: C, 64.45, 64.48; H, 3.41, 3.45; N, 17.61, 17.79%.

Condensation of Phenylacetaldehyde with Sodium Cyanoacetate

To a solution of sodium cyanoacetate prepared from 25 gm. of mono-chloracetic acid were added 15 gm. of phenylacetaldehyde, 15 cc. of alcohol, and 30 cc. of strong sodium hydroxide solution. The mixture was shaken vigorously for five minutes and allowed to stand. The reaction yielded 15.3 gm. of an acidic oil from which αα'-dicyano-β-benzylglutaric acid was separated through its soluble copper salt. The remaining oil recovered from the insoluble copper salt contained two acids which were separated as their barium salts, one being insoluble, the other soluble, in water. The acids liberated from their barium salts failed to produce 1-hydroxy-2-naphthoic nitrile when distilled *in vacuo*.

Oxidation of Phenylacetaldehyde

A solution of phenylacetaldehyde (1 gm.) in 5 cc. of glacial acetic acid was treated with 4 gm. of chromic acid in 15 cc. of glacial acetic acid. After the vigorous reaction had subsided the mixture was heated for half an hour and then poured into 200 cc. of water. The solution was extracted with

ether and the extract washed free of acetic acid with water. The residue left after distillation of the ether was boiled with a little water, and the solution, decanted from some insoluble oil, yielded shiny white plates, m.p. 120°C. The product did not depress the melting point of a sample of pure benzoic acid (m.p. 122° C.) when admixed with it.

Ozonization of Neutral Condensation Product

Through a solution in chloroform of 2 gm. of the neutral product of the condensation of phenylacetaldehyde with ethyl cyanoacetate a stream of ozonized oxygen was passed for 85 hr. The ozonized substance was then freed of chloroform and treated on the water bath with 25 cc. of 6% sulphuric acid and 3 gm. of potassium ferrocyanide. This yielded a neutral fraction, which, when treated with semioxamazide, failed to disclose the presence of an aldehyde.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LIII. STRUCTURE OF THE DEXTRAN SYNTHESIZED BY THE ACTION OF LEUCONOSTOC MESENTERIOIDES ON SUCROSE[1]

By Frances L. Fowler[2], Irene K. Buckland[2], Fritz Brauns[3], and Harold Hibbert[4]

Abstract

The dextran synthesized from sucrose by the action of one strain of *Leuconostoc mesenterioides* has been subjected to chemical investigation. The polysaccharide has been hydrolyzed to glucose. The triacetate, tribenzoate, and trimethyl derivative (all calculated on a glucose anhydride unit) have been prepared. Hydrolysis of trimethyl dextran by the action of methanol-hydrochloric acid yielded dimethyl, trimethyl, and tetramethyl methyl glucosides in the ratio of 1 : 3 : 1. The products of hydrolysis have been identified as 2,3-dimethyl methyl glucoside, 2,3,4-trimethyl methyl glucoside, and 2,3,4,6-tetramethyl methyl glucoside.

The results indicate that dextran is a polymer of a pentaglucopyranose anhydride. One of the glucopyranose units is attached as a side chain, the remaining four being most probably connected in linear chain union. Three of the linkages between building units are of the 1,6 type, while the remaining two are either 1,4 or 1,6.

The antigenic properties shown by dextran are probably a result of the presence of the glucose side chains.

Introduction

The present investigation represents one of a systematic series of studies begun several years ago by Hibbert and co-workers on the polysaccharides elaborated by certain species of bacteria. Previous communications (6, 9, 10, 11, 16, 23) have dealt with the synthesis and structure of bacterial levans and celluloses. Furthermore, the nature of the synthesis of dextran from sucrose by the action of *Leuconostoc mesenterioides* was investigated by Tarr and Hibbert (24). As noted by these authors, the occurrence of dextran has been reported in connection with the wine and sugar industries since the time of Pasteur. It was identified by Scheibler (19, 20) as an anhydride of dextrose, and shown by Jubert (13) to be a product of fermentation of sugar solutions.

In recent years the polysaccharides elaborated by bacteria have assumed a position of great importance in the field of immuno-chemistry. The numerous researches of Avery, Heidelberger, and many others have shown that specific polysaccharides are responsible for type specificity and virulence of many

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pathogenic bacteria, and considerable advances have been made in the correlation of specificity with chemical structure.

Preliminary investigations by FitzGerald (5) and by Zozaya (26, 27, 28) have indicated that dextran possesses a certain degree of immunological specificity. Its structure, therefore, becomes a problem of interest, not only to the carbohydrate chemist, but also to the immunologist.

Previous chemical investigations relating to the structure of dextran have been very limited in scope. As mentioned above, Scheibler (19, 20) showed that it was an anhydride of glucose, and his results were confirmed by Jubert (13) and later by Browne (2). Däumichen (4) found that the product formed a triacetate and a tribenzoate; this indicated the presence of three free hydroxyl groups for each glucose-anhydride unit in the molecule.

Up to the present, however, the manner of linkage of the glucose anhydride units with each other has not been determined. In 1931, Tarr and Hibbert (24) intimated that the structure of the polysaccharide was being investigated in these laboratories. The problem has, however, proved difficult of solution, owing in part to the complex nature of the structure, and in part to the great difficulty encountered in effecting a complete methylation of the product.

Discussion of Results

The dextran under consideration was produced by the action on sucrose of *Leuconostoc mesenterioides*, "Culture 4", as described by Tarr and Hibbert (24).

When purified by electrodialysis the product was obtained as a pure white powder, free from nitrogen, and containing only 0.07% ash. The empirical formula, determined by combustion analyses, was $(C_6H_{10}O_5)_x$.

Hydrolysis of dextran with dilute sulphuric acid gave a 90% yield of glucose. The formation of a triacetate and a tribenzoate (calculated on a glucose-anhydride unit) was confirmed.

Methylation by means of dimethyl sulphate and alkali, as well as silver oxide and methyl iodide, resulted in a methoxyl content of only 40 to 41% (theoretical 45.6%). This value was increased to 43.3% by the use of thallium ethylate and methyl iodide, but the polysaccharide proved extremely resistant to further methylation.

A methoxyl content of 45.4% was finally obtained by a slight modification of the method of Muskat (17,18), which consists in first forming the sodium or potassium derivative in liquid ammonia, followed by treatment with a methylating agent such as methyl iodide.

The completely methylated product, on hydrolysis with hydrogen chloride in absolute methanol, yielded, on fractionation, a mixture of dimethyl, trimethyl, and tetramethyl methyl glucosides in the ratio of 1 : 3 : 1. The tetramethyl methyl glucoside, on hydrolysis, yielded crystalline 2,3,4,6-tetramethyl glucose. This showed that this unit is present in the pyranose form

in the original polysaccharide, and that it is linked to the rest of the molecule through carbon atom 1. The latter fact finds confirmation in the non-reducing character of the dextran, which indicates that all the reducing groups in the building units are chemically linked.

From the trimethyl fraction, crystalline 2,3,4-trimethyl-β-methyl glucoside was isolated. This proved that the hydroxyl groups in positions 2, 3, and 4 are free in the original polysaccharide, and that the original ring structure is of the pyranose form.

Treatment of the dimethyl methyl glucoside with trityl chloride yielded crystalline 2,3-dimethyl-6-trityl-α-methyl glucoside. In this fraction, therefore, the hydroxyl groups on carbon atoms 2 and 3 were free in the original polysaccharide. No conclusions can be drawn regarding the ring structure of this unit, since, although the glucoside is of the pyranose form when isolated, the possibility of ring shift from carbon atom 4 to carbon atom 5 during hydrolysis has not been excluded in this case. However, because the pyranose form has been shown to be present in the other units of the polysaccharide, and since no naturally occurring glucofuranose compounds are known, a uniform glucopyranose structure for all units seems highly probable.

On the basis of the evidence cited above, two tentative formulas for dextran, differing only in the position of attachment of the side chain, may be put forward.

It can readily be seen, however, that Formulas I and II do not exhaust all the possibilities for the structure of dextran on the basis of the present experimental evidence. It is possible that the side chain may consist of two, three, or even four units, with a corresponding shortening of the primary chains.

(I)

$$CH_2OH$$
$$CH$$
$$HOCH$$
$$O \quad HCOH$$
$$HOCH$$
$$CH$$

- - - O
CH—   CH—   CH—   CH—
HCOH   HCOH   HCOH   HCOH
HOCH O O HOCH O O HOCH O O HOCH O O
HCOH   HCOH   HCOH   HC—
HC—   HC—   HC—   HC—
CH₂—   CH₂—   CH₂—   CH₂ - - - - - -

(II)
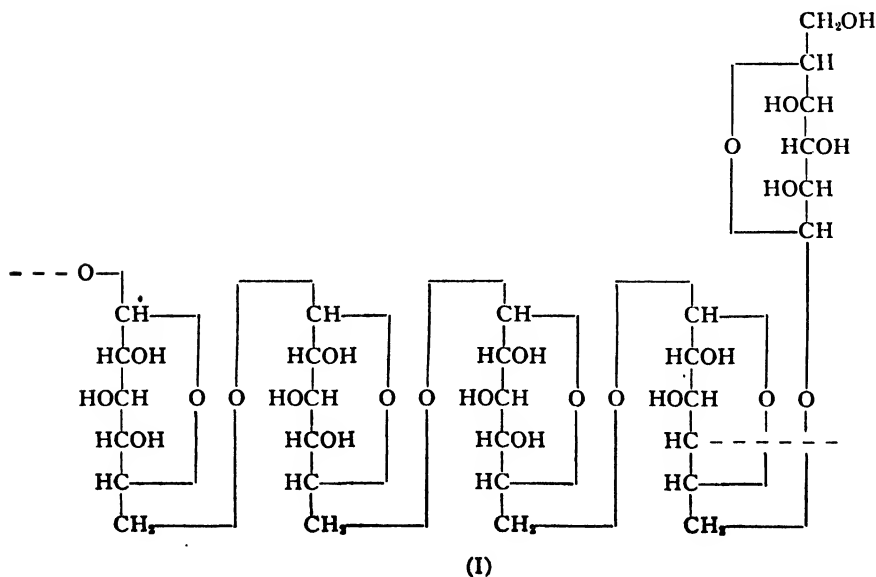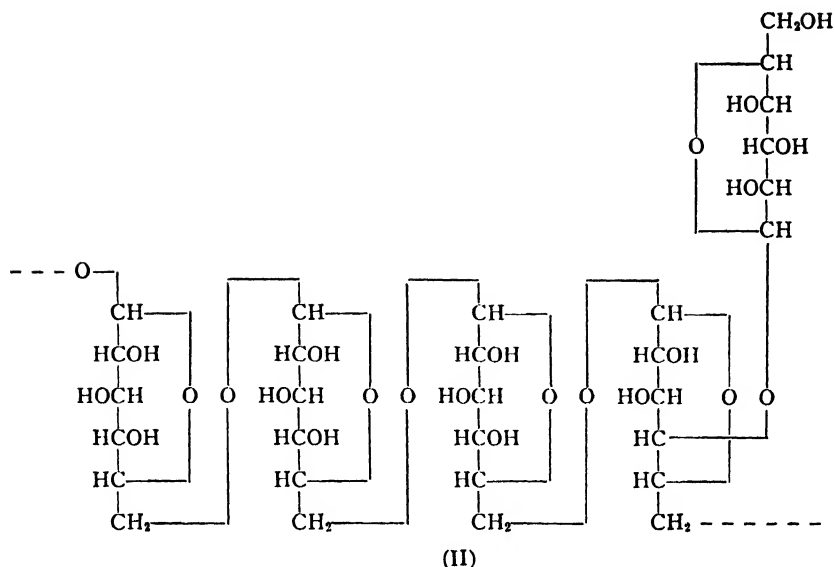
The same problem is presented in the case of the recently investigated polysaccharide, graminin. The formula suggested by Schlubach and Koenig (21) for this product is the ring structure, A.

A   *B*
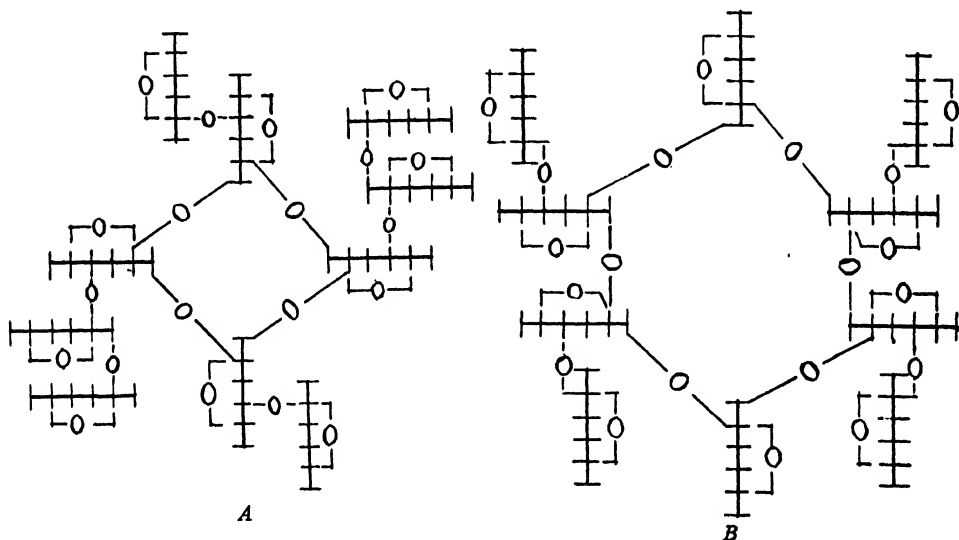
This formula was deduced from the facts that the polysaccharide is non-reducing, has a molecular weight corresponding to 10 fructose units, and, on methylation and hydrolysis yields dimethyl, trimethyl, and tetramethyl methyl fructosides in the ratio 2 : 1 : 2. It is evident, however, that the larger ring, B, in which the side chains of only *one* unit are all similar, would explain the facts equally well.

Antigenic Properties of Dextran

Recent investigations on the bacterial polysaccharides have indicated the importance of their specific immunological role (pneumococcus, etc.), and the fact that dextran has a marked antigenic character would seem to point to this latter action as due to the presence therein of the glucose side chain.

In this connection it is of interest that a yeast polysaccharide shown previously by Kesten, Cook, Mott, and Jobling (14) to have antigenic properties has now been isolated by Sevag, Cattanio, and Mauweg (22). It has an acetyl content of about 9% and is precipitated by the antiserum of Type 2 pneumococcus (0.01% solution). Furthermore, Haworth, Hirst, and Isherwood (7) found that the yeast polysaccharide isolated by them by alkaline extraction also contains side chains of a hexose unit.

The antigenic action shown by dextran was found by FitzGerald and co-workers to disappear when the nitrogen content fell below 0.2%. In view, however, of the decisive antigenic role played by a small percentage of acetyl in certain polysaccharides, as shown quite recently by Avery and Goebel (1), it is possible that the negative action found by FitzGerald and co-workers (5) may be due to the removal of acetyl groups arising in the final purification of the dextran carried out in these laboratories.

These questions are now the subject of investigation by E. C. Fairhead.

Experimental

Purification of Dextran by Electrodialysis

Dextran (20 gm.) prepared according to the method of Tarr and Hibbert (24) was dissolved in 500 cc. of 0.4 N sodium hydroxide solution, and electrodialyzed (potential, 110 volts) in the Pauly apparatus for one week against distilled water. The solution was then poured in a fine stream, with vigorous mechanical stirring, into three times its volume of anhydrous methanol.

The resulting flocculent white precipitate was free from reducing sugars and nitrogen. Ash, 0.07%. $\alpha_D = +198.3°$ in 1.117 N sodium hydroxide solution, $c = 1.86\%$. Found (microanalysis): C, 44.6; H, 6.30%. Calcd. for $(C_6H_{10}O_5)_x$: C, 44.5; H, 6.18%.

Hydrolysis of Dextran with Dilute Sulphuric Acid

Dextran (1.0 gm.) was dissolved in 15 cc. of water and 10 cc. of 70% sulphuric acid was added slowly, while cooling with ice. After standing for four days at 36° C. the solution was clear and colorless. It was then diluted to 100 cc. and heated in a boiling-water bath. After six hours the rotation was constant. The solution was neutralized with barium carbonate, decolorized with charcoal, filtered, evaporated under reduced pressure to a thick syrup, and the syrup dissolved in hot absolute ethanol. On cooling, 1.0 gm. of white crystals was obtained, which, on further recrystallization from ethanol, gave $\alpha_D = +51.2°$. The product formed an osazone; m.p. 204.5 to 205° C. [*]

[*] Melting points are not corrected.

In order to obtain a quantitative estimation of the yield of glucose, the method of Willstätter and Schudel (25) was employed. By this method, dextran, (0.5688 gm.) gave, on hydrolysis, a 90.5% yield of glucose (0.5710 gm.).

Benzoylation of Dextran

Anhydrous dextran (1 gm.) was dissolved in 19 cc. of dry quinoline and 4.5 cc. of benzoyl chloride added. The mixture was heated for three hours at 120° to 130° C., whereupon there was formed a thick gel, which solidified on cooling to a light-brown mass. This was dissolved in chloroform, and the solution extracted successively with water, 5% sulphuric acid, water, saturated sodium bicarbonate solution, and again with water. The pale red solution was dried over sodium sulphate, then centrifuged and evaporated under reduced pressure to a volume of 50 cc. It was poured slowly, with stirring, into absolute methanol, and the resulting finely divided white precipitate washed with absolute methanol, then with petroleum ether, and vacuum dried over sulphuric acid and potassium hydroxide. $\alpha_D = +193.7°$ in acetylene tetrachloride, $c = 2.44\%$. Found: C_6H_5CO, 64.67%. Calcd. for $C_6H_7O_5(C_6H_5CO)_3$: C_6H_5CO, 66.45%.

Acetylation of Dextran

Preliminary experiments showed that dextran does not dissolve in dry pyridine at 80° C., so that use of aqueous pyridine solution was necessary.

Dextran (2 gm.) was suspended in 20 cc. of pyridine containing 4 cc. of water and stirred vigorously for several hours. Approximately half the dextran appeared to dissolve. Further quantities of pyridine (25 cc.) and acetic anhydride (33 cc.) were added with continuous stirring over a period of three hours at room temperature. The mixture was then stirred and heated for four hours at 50° C. and one hour at 80° C. The insoluble product was removed by centrifuging, and the supernatant liquor poured on to cracked ice. Only a very flocculent precipitate formed. The product remaining in the centrifuge jar was washed with water and vacuum dried. Yield, 2.7 gm. (79%). Found: CH_3CO, 44.1%. Calcd. for $C_6H_7O_5(CH_3CO)_3$: CH_3CO, 44.8%.

Methylation of Dextran*

Dextran (24 gm.) was methylated with 80 cc. of dimethyl sulphate and 196 cc. of 50% potassium hydroxide in the usual manner, and the resulting solution dialyzed until free from sulphates. A small portion was poured into acetone and the precipitated product separated and analyzed (OCH_3, 12.8%). The methoxyl content was increased to 30.7% by a second methylation.

The precipitated dextran was now dissolved in 200 cc. of dry anisol**, and the solution frozen by immersion of the reaction flask in a mixture of

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*Procedures involving the use of silver oxide and methyl iodide, and of thallium ethylate and methyl iodide which resulted in incomplete methylation of other samples of dextran are not described.

**The application of this solvent, which has been used in this laboratory for the last few years, has recently been described by Hess (8).

dry-ice and acetone at −50° C. Dry ammonia (100 cc.) was condensed on the frozen mass and 3 gm. of sodium dissolved in it. The temperature of the bath was raised to −35° C., which is between the melting point of anisol and the boiling point of ammonia. After the anisol solution had melted it was shaken thoroughly with the ammonia solution. The ammonia was then allowed to evaporate, the last traces being removed by distilling off a portion of the anisol under reduced pressure.

Methyl iodide (15 cc.) was added, and the solution refluxed overnight at 40° C. After removal of the anisol by distillation, the residue was dissolved in approximately 500 cc. of water and dialyzed. After removal of the water, the product was dissolved in chloroform and precipitated in low-boiling petroleum ether. The methoxyl content was now 41.9%. After a total of five methylations by this method the methoxyl content was 45.4%. $[\alpha]_D^{21°} = +202.2°$ in acetylene tetrachloride, $c = 0.758\%$. Found (microanalysis); C, 52.81; H, 7.73; OCH₃*, 45.4%. Calcd. for $C_6H_7O_2(OCH_3)_3$, C, 53.0: H, 7.85; OCH₃, 45.6%.

Hydrolysis of Fully Methylated Dextran

Fully methylated dextran (12.0 gm.) was heated in a sealed tube with a solution of 1.5% by weight of anhydrous hydrogen chloride in 150 cc. of absolute methanol. The heating was carried out in a tilting-oven, for 24 hr. at 125° C., then for 24 hr. at 145° to 150° C. After this time the dextran had completely dissolved, and the solution was clear and light-yellow.

The product was freed from hydrochloric acid by shaking it for two hours with 30 gm. of silver carbonate. After the solution had been filtered through charcoal it was shaken for 12 hr. with charcoal, to remove traces of silver salts, and filtered.

The clear, colorless solution was evaporated at a pressure of 15 mm. to a pale yellow syrup; weight, 12.05 gm. (87% of the calculated yield). The syrup did not reduce Fehling's solution. Its methoxyl content corresponded to that of trimethyl methyl glucoside. Found (microanalysis): OCH₃, 52.2%. Calcd. for $C_6H_8O_2(OCH_3)_4$: OCH₃, 52.6%.

The syrup distilled between 75° and 125° C. (pressure 0.01 mm., bath temperature, 95° to 170° C.). The first portion of the distillate, a colorless mobile oil, was followed by a viscous pale yellow syrup. A methoxyl determination on the last portion of the distillate gave a value corresponding to dimethyl methyl glucoside. OCH₃ = 42.1%. Calcd. for $C_6H_9O_3(OCH_3)_3$: 41.9%. Since the methoxyl content of the original mixture was that of a trimethyl methyl glucoside, it is apparent that dimethyl and tetramethyl methyl glucosides were present in equivalent amounts.

Separation of the Hydrolysis Products of Fully Methylated Dextran

A portion (7.5 gm.) of the original hydrolysis products (OCH₃, 52.2%) was dissolved in 100 cc. of water, and the solution exhaustively extracted with chloroform according to the procedure of Macdonald (15). The aqueous

All analyses for methoxyl content were made by the Vieböck and Schwappach method as described by Clark (3).

TABLE I

PRODUCTS OF HYDROLYSIS OF FULLY METHYLATED DEXTRAN

Product	Yield from 7.5 gm. of hydrolytic products, gm.	Corrected yield, gm.	Calcd. for 1 : 1 : 1 ratio		Calcd. for 1 : 2 : 1 ratio		Calcd. for 1 : 3 : 1 ratio		Calcd. for 1 : 4 : 1 ratio	
			Theor. yield, gm.	Yield, %	Theor. yield, gm.	Yield, %	Theor. yield, gm.	Yield, %	Theor. yield, gm.	Yield, %
Dimethyl methyl glucoside (mol. wt. 222.15)	1.40	1.70	2.35	59.6	1.76	79.5	1.41	99.3	1.18	119.0
Trimethyl methyl glucoside (mol. wt. 236.16)	3.57	4.34	2.50	141.0	3.75	94.0	4.50	78.3	5.0	70.5
Tetramethyl methyl glucoside (mol. wt. 250.18)	1.20	1.17	2.65	45.3	1.99	60.3	1.59	75.5	1.32	91.0

solution (containing the dimethyl methyl glucoside), on evaporation under reduced pressure, yielded a light-brown, viscous syrup. Yield, 1.35 gm. The separation of the glucosides constituting the chloroform soluble fraction was carried out by fractional distillation under high vacuum, as shown schematically in Fig. 1. All fractions were controlled by determinations of refractive index, in order to obviate the possibility of contamination of the trimethyl fraction with equal parts of the dimethyl and tetramethyl derivatives.

From the methoxyl contents of the various fractions, it is evident that fractions Va and Vb consist essentially of tetramethyl methyl glucoside, IVc, and IVd of trimethyl methyl glucoside, and IIf and IVe of dimethyl methyl glucoside. The total amount of trimethyl methyl glucoside from the original 7.5 gm. of hydrolytic products was 3.57 gm. (made up of 2.03 gm. of fractions IVc, IVd, Vc, and 1.54 gm. of crystalline material isolated from fractions IIb and IIc), equivalent to a yield of 47.6%. The yields of dimethyl and tetramethyl methyl glucosides (Fractions IIf+IVe and Va+Vb respectively) were 1.40 and 1.20 gm., equivalent to 18.7 and 16% respectively. The working-loss thus amounts to $7.5-6.17=1.33$ gm. or 17.3%. If this loss, in accordance with accepted experimental practice, is allocated *pro rata* to the three fractions, the corrected yields are 1.70, 4.34, and 1.47 gm. respectively. This clearly identifies dextran as the 1 : 3 : 1 polymer.

This ratio of dimethyl methyl glucoside : trimethyl methyl glucoside : tetramethyl methyl glucoside was confirmed by the following experiment.

Check on the Yield of Trimethyl Methyl Glucoside by Hydrolysis to Trimethyl
*   Glucose*

A portion of the original glucoside hydrolytic products (4.55 gm.) was dissolved in 100 cc. of water, and the trimethyl and tetramethyl methyl glucosides were removed by chloroform extraction as before. The chloroform solution, on evaporation, yielded a pale yellow syrup. $n_D = 1.455$, corresponding approximately to a mixture of 25% of tetramethyl and 75% of trimethyl methyl glucosides. Yield, 3.85 gm.

This syrup was dissolved in 250 cc. of 5% aqueous hydrochloric acid (according to the procedure of Irvine and Oldham (12)). The mixture was heated under reflux on a water bath at 90° to 95° C. for nine hours, after which time the rotation was constant.

The acid solution was extracted five times with 125-cc. portions of chloroform. The combined extracts, on evaporation, yielded 0.575 gm. of a light-yellow syrup, which crystallized on inoculation with a crystal of 2,3,4,6-tetramethyl glucose.

The aqueous solution was neutralized by shaking with silver carbonate, filtered, and shaken overnight with charcoal. On filtration and evaporation under reduced pressure, the solution yielded a viscous syrup that was dark in color owing to the presence of silver salts. Yield, 2.38 gm.; OCH$_3$, 38.2%. Since the methoxyl content of trimethyl glucose is 41.9%, the actual yield

Fully methylated dextran hydrolyzed with CH_3OH and HCl (7.5 gm. hydrolytic products used)

Sol'n in H_2O and extraction with $CHCl_3$

FIG. 1
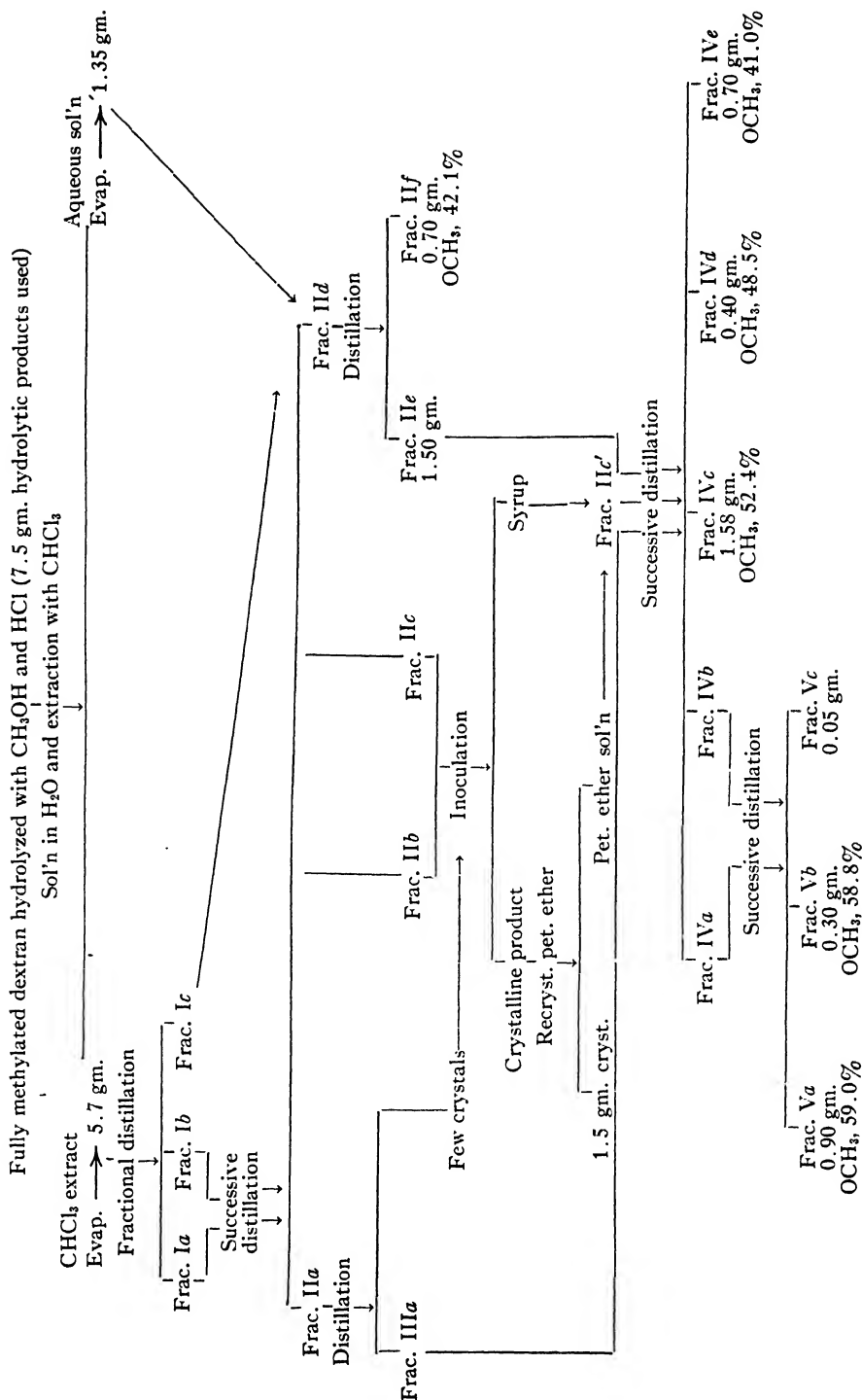
of the sugar calculated on the basis of methoxyl content is 93% of the 2.38 gm. obtained. This product contained no dimethyl glucose, since shaking in acetone solution with charcoal, filtering, and evaporating yielded a thick colorless syrup: OCH_3, 41.4%.

The yield of 2.38 gm. of crude product, of 93% purity, thus corresponds to 2.21 gm. of pure trimethyl glucose, or 2.35 gm. of trimethyl methyl glucoside, equivalent to 52.3% of the original mixture.

The theoretical yield, calculated on a 1 : 3 : 1 basis is 60%, whereas on a 1 : 2 : 1 basis it is only 50%. The yield obtained thus represents 87% of the theoretical yield for trimethyl methyl glucoside represented in the 1 : 3 : 1 ratio, and is in excess of that required by a 1 : 2 : 1 ratio.

Identification of the Dimethyl Methyl Glucoside

The dimethyl methyl glucoside obtained in fraction IVe (Fig. 1) was redistilled, and obtained as a colorless viscous syrup, b.p. 100° to 105° C. (pressure, 0.003 mm.; bath temperature, 125° to 130° C.). Found (by micro-analysis: C, 49.9; H, 8.09; OCH_3, 41.4%. Calcd. for $C_6H_9O_3(OCH_3)_2$: C, 48.8; H, 8.12; OCH_3, 41.9%.

A portion (0.5 gm.) of the above product and 0.63 gm. of trityl chloride were dissolved in 4 cc. of dry pyridine and heated for one hour in a boiling water bath. The solution was cooled, the precipitated pyridine hydrochloride removed by filtration, and the filtrate then poured, with stirring, into 50 cc. of ice-water whereupon a pale yellow sticky mass was precipitated. This solidified on standing overnight in the ice box.

The resulting granular precipitate was filtered, washed, and vacuum dried over phosphorus pentoxide at 100° C. After two crystallizations from absolute ethanol, it was obtained in the form of rhombic plates, m.p. 168.5° to 169.5° C. (corrected). The mixed melting-point with a synthetic specimen of 2,3-di-methyl-6-trityl-α-methyl glucoside was 167.5° to 169.5° C. Found (by microanalysis): C, 72.4; H, 7.05; OCH_3, 20.3%. Calcd. for $C_6H_8O_2$ $(OCH_3)_3 . OC(C_6H_5)_3$: C, 72.5; H, 6.91; OCH_3, 20.0%.

Identification of the Trimethyl Methyl Glucoside

During the fractional distillation of the products of hydrolysis, approximately one-half of the trimethyl methyl glucoside was obtained in crystalline form. After the crystals had been pressed on a porous plate and recrystallized three times from low-boiling petroleum ether they were obtained as a mass of white needles. The product was then further purified three times by sublimation at 80° C. at 15 mm. M.p., 94° C. The mixed melting point with a specimen of 2,3,4-trimethyl-β-methyl glucoside* was 94° C. $[\alpha]_D^{20°} = -20.57°$ in chloroform, $c = 3.325\%$. Found (microanalysis): C, 50.46; H, 8.35; OCH_3, 52.0%. Calcd. for $C_6H_8O_2(OCH_3)_4$: C, 50.9; H, 8.49; OCH_3, 52.6%.

*Received through the kindness of Sir James Irvine of the University of St. Andrews.

Identification of the Tetramethyl Methyl Glucoside

A portion (0.5 gm.) of Fraction V*a* (Fig. 1) was dissolved in 50 cc. of 5% aqueous hydrochloric acid and heated on a water bath at 90° to 95° C. After four hours the rotation was constant.

The acid solution was extracted with five 25 cc. portions of chloroform, and the combined chloroform extracts were evaporated under reduced pressure to a pale yellow syrup. On inoculation with a crystal of 2,3,4,6-tetramethyl glucose, the syrup crystallized.

The product was recrystallized three times from low boiling petroleum ether containing a trace of ether, and obtained as a mass of fine white needles; m.p., 86° to 88° C. When mixed with a specimen of 2,3,4,6-tetramethyl glucose (prepared by hydrolysis of octamethyl maltose) melting at 88° to 90° C., the mixture melted at 86° to 89° C. $[\alpha]_D^{21°} = +105.4°$ in chloroform, $c = 0.587\%$. No mutarotation was observed in the course of 36 hr. Found (microanalysis): C, 50.8; H, 8.41; OCH$_3$, 51.9%. Calcd. for C$_6$H$_8$O$_2$(OCH$_3$)$_4$. C, 50.9; H, 8.49; OCH$_3$, 52.6%.

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THE PHOTODECOMPOSITION OF CHLORINE DIOXIDE IN CARBON TETRACHLORIDE SOLUTION[1]

BY J. W. T. SPINKS[2] AND H. TAUBE[3]

Abstract

Insolation of carbon tetrachloride solutions of chlorine dioxide initiates a thermal decomposition, the magnitude of which may exceed that for the photo-reaction with low light intensity. This thermal decomposition is inhibited by keeping the solutions at 3° C. or by adding water.

In contradiction to the findings of other investigators, it is found that chlorine and oxygen are not the only products of photodecomposition. As products of the photodecomposition of chlorine dioxide at the wave-lengths 3650 and 4360 Å, the oxides Cl_2O, Cl_2O_6, and Cl_2O_7 as well as chlorine and oxygen appear. The quantum efficiency at λ 3650 Å is 2, and at 4360 Å, 1.

In the unsensitized decomposition, concentration effects are observed which are greatly decreased when the solutions are stirred.

In the bromine sensitized decomposition with 5460 Å, there is less chlorine monoxide but relatively as much Cl_2O_6 and Cl_2O_7 formed as in the unsensitized reaction.

In the sensitized decomposition the quantum yield is independent of the concentration of chlorine dioxide, but depends on the light intensity. The observed quantum yield for the sensitized reaction is 0.2 to 0.3.

Mechanisms for the photo-reactions have been proposed.

Introduction

Gaseous chlorine dioxide decomposes at a measurable rate above 30° C., but at temperatures of from 50° to 60° C., the decomposition proceeds explosively; Cl_2O_6 is an intermediate product in the thermal decomposition (26). Luther and Hoffmann (15, 16) have made a study of the thermal decomposition of chlorine dioxide in carbon tetrachloride solution. Pure chlorine dioxide solutions were found to be stable in the dark; previous insolation or the addition of chlorine monoxide initiates a slow thermal decomposition.

In the visible region of the spectrum, chlorine dioxide shows band absorption that begins at 5225 Å and continues to 2000 Å (8, p. 709; 28). At 3750 Å the lines become diffuse; this indicates predissociation. The bands may be extrapolated to a convergence limit at 2560 Å, corresponding to a dissociation of the chlorine dioxide to ClO + O(^{1}D). The energy required for the dissociation

$$ClO_2 \longrightarrow ClO + O(^3P)$$

corresponds to a wave-length 4360 Å. It is of course possible that predissociation takes place up to 4360 Å even though diffuse bands are not observed.

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On insolation of gaseous chlorine dioxide, Booth and Bowen (3) obtained a brown liquid which was later identified as Cl_2O_6 (2). Finkelnburg and Schumacher (8, p. 709) investigated the reaction, using λ 4360 and 3130 Å.

Spinks and Porter (27, p. 269) found the photodecomposition with dry gases to be complicated. A chain mechanism was indicated since the quantum yield was found to be about 12. By using moist gases, results were reproducible, since active groups, presumed to be ClO_3, ClO, and Cl_2O_3, were then removed by the water. With moist gases and wave-lengths 4360 and 3650 Å, quantum yields of 3.1 and 3.7, respectively, are obtained. For the bromine sensitized reaction, with moist gases and λ 5460 Å, the quantum yield was found to be equal to the yield when 3650 Å was used.

In carbon tetrachloride solutions, using blue and violet light, Bowen (4) found $\gamma = 1$, but the light measurements were not very accurate. A slight thermal reaction was reported. Nagai and Goodeve (17), using λ 4100 to 4200 Å, obtained a quantum yield of 2. They observed a rapid thermal reaction and made their calculations on the assumption that the thermal and photo-reactions proceed independently. In contrast to the reaction in the gas, it was claimed that no Cl_2O_6 is formed. Bowen (5) and Bowen and Cheung (6) repeated the study with carbon tetrachloride and water solutions, and used light of wave-length varying from 3000 to 4360 Å. In carbon tetrachloride, the quantum yield was found to be equal to 2 up to 4200 Å; at 4360 Å it was found to be 1; for water solutions it increased from 0.2 at a wave-length of 4360 Å to 1 for λ 3000 Å.

Since the line 5460 Å does not possess sufficient energy to cause the dissociation

$$ClO_2 \longrightarrow ClO + O$$

it was hoped that by studying the bromine sensitized decomposition, using this wave-length, further significant information about the photodecomposition of chlorine dioxide might be obtained. Since our experiments differed in important respects from published work on the subject of the photodecomposition of chlorine dioxide, the original study was extended to include the unsensitized decomposition with wave-lengths 4360 and 3650 Å.

The work reported here embraces a study of the thermal decomposition, an investigation of the reaction products of the photodecomposition, measurement of the quantum yield, and a study of the influence of light intensity and of concentration of the reactants on the rate of decomposition.

Experimental

Preparation of Materials

Carbon Tetrachloride. U.S.P. carbon tetrachloride was filtered, shaken with concentrated sulphuric acid, washed with alkali, and dried with calcium chloride. Chlorine dioxide was passed in and the solution exposed to light from a 100 watt bulb for a period of about four days, more chlorine dioxide being passed in as it was decomposed. The chlorine and chlorine dioxide were then washed out with concentrated alkali and the carbon tetrachloride

was dried over phosphorus pentoxide. After drying for some time, it was distilled in an all-glass apparatus from phosphorus pentoxide, the end fractions being discarded.

Untreated U.S.P. carbon tetrachloride, as well as Mallinckrodt's c.p. carbon tetrachloride showed anomalous effects. In runs with such carbon tetrachloride, thermal decomposition at 3° C., large change in total halogen (calculated as described below) and large decrease in light absorption were noticed. All batches of carbon tetrachloride subjected to a rigorous treatment with chlorine dioxide gave comparable results.

Bromine. In the earlier experiments, a c.p. grade of bromine was used. For the later work, this grade of bromine was treated by distilling from potassium bromide and potassium bromate and from phosphorus pentoxide. No difference in the results obtained by using either grade of bromine could be observed.

Chlorine Dioxide. This gas was prepared by the method of Bray (7). Potassium chlorate (3 gm.) and crystalline oxalic acid (12 gm.) were ground in a mortar, and 1.5 cc. of water was added. The mixture was then heated at a temperature of 55° to 65° C. The gas evolved was bubbled through saturated sodium bicarbonate, pre-dried with sulphuric acid, then passed over phosphorus pentoxide into dry, purified carbon tetrachloride. In all cases the chlorine dioxide contained about 2 mole per cent of chlorine. The solutions were prepared just before use and were kept, carefully shielded from light, at 0° C.

Apparatus

The light source was a constant pressure, quartz mercury lamp, consuming 1.8 amp. at 220 volts. For some experiments a vacuum quartz mercury lamp consuming 2.5 amp. was used. The light from the latter is very intense but flickers excessively. The light filters employed were: for 5460 Å, a combination of Corning Nonex, heat resisting yellow, 2.8 mm. thick, and a Corning Didymium glass 4.97 mm. thick; for 3650 Å, a Corning red purple ultra filter, 3.9 mm. thick; for 4360 Å a cobalt glass and 2 cm. of a solution of 40 gm. of sodium nitrite in 100 cc. of water.

For the experiments on quantum yields, where accurate light measurements are necessary, the optical arrangement shown in Fig. 1 was used. The arrangement of lenses and apertures was such that a fairly homogeneous beam, slightly convergent, with a cross section at the face of the thermopile of 1.5 cm. in diameter, was obtained. The light measuring instrument was a Moll surface thermopile (receiving cone stepped down, active surface 2 cm. in diameter) connected in series with a sensitive galvanometer.
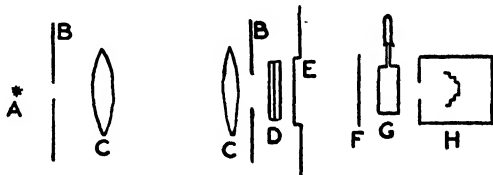
FIG. 1. *A, mercury lamp; B, apertures; C, lenses; D, filters; E, bath; F, shutter; G, cell; H, thermopile.*

Deflections were read by means of an optical lever, radius 1.2 m. The thermopile was calibrated against two Bureau of Standards carbon filament lamps. One millimetre of deflection corresponds to 1.14×10^{-5} watts falling on the face of the thermopile. The calibration and optical systems were checked by measuring the quantum yield of the uranyl oxalate decomposition with λ 3650 Å, the value for this reaction being accurately known (28). The results obtained are described under the heading "Measurement of the Quantum Yield."

For the other experiments, in order that there would be a measurable decomposition in a short time, a more intense beam was used. This was obtained by condensing the light from the lamp, without a diaphragm, by means of a 500 cc. Pyrex flask, filled with water and at a distance of 2 cm. from the lamp, and a lens at a distance of 1 or 2 cm. from the flask.

The reaction cell employed was of Suprax glass, 2 cm. in thickness and 5 cm. in diameter, fitted with a ground glass cap, and over this a tube and stopper to exclude water. The volume of the cell was about 29.5 cc. The bulbs used to determine the initial concentration and the thermal change were blown from soft glass, and were also fitted with ground glass caps. The joints were sparingly lubricated with a brominated grease. Experiments showed that there was no loss of oxidizing material over a 24-hr. period.

For the low temperature work, the solutions were exposed to the light in a small insulated bath fitted with two glass windows. Ice was kept on the surface of the water and the cell was thus maintained at a temperature of about 3° C.

Procedure and Method of Analysis

The chlorine dioxide solution, prepared as described above, was dispensed from the containing vessel into the cells by means of dry compressed air. In the early runs, when the conditions under which the thermal change took place were being studied, three portions were used: one to obtain the initial concentration, one to measure the thermal change, and one to measure the change on insolation. The amounts of solution used were obtained by weighing.

To analyze the solutions, the liquid was forced into potassium iodide solution by means of a siphon. All oxidizing material was removed by blowing with dry compressed air. To the resulting solution was added standard acid in excess of that required in Reaction (1).

$$ClO_2 + 5KI + 2H_2SO_4 \longrightarrow KCl + 2K_2SO_4 + 2\tfrac{1}{2}I_2 + 2H_2O \qquad (1)$$

$$Br_2 \text{ (or } Cl_2) + 2KI \longrightarrow 2KBr + I_2 \qquad (2)$$
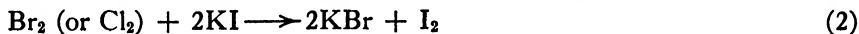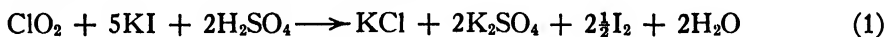
The iodine liberated in these reactions is determined by titration with 0.1 N sodium thiosulphate. Reaction (1) uses up acid quantitatively; thus the chlorine dioxide can be obtained from the amount of acid which disappeared. If this result is compared with the total iodine liberated, the amount of chlorine

plus bromine may be obtained. The excess acid was determined by adding excess potassium iodate, and Reaction (3) takes place.

$$\cdot KIO_3 + 5KI + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3I_2 \tag{3}$$

The liberated iodine was again titrated with 0.1 N sodium thiosulphate and gave a measure of the excess acid which had been added. Thus the amount of acid used in Reaction (1) could be calculated.

Throughout this report, the chlorine dioxide used in a run, the amount left after decomposition, and the amount decomposed is expressed in terms of the corresponding titre for 0.1 N sodium thiosulphate divided by 5. Multiplying by 10^{-4} gives the actual number of moles of chlorine dioxide involved. The chlorine and bromine are expressed in terms of the 0.1 N sodium thiosulphate titre. These units are adopted since equal titres then represent equal amounts of halogen.

The following was used as a check on the analysis. For the same weight of solution in each of the cells,

$$\frac{ClO_2 \text{ titre}}{5} + (Cl_2 + Br_2) \text{ titre},$$

(both in cubic centimetres of 0.1 N sodium thiosulphate) should be a constant, since this represents the total halogen present, none of which is lost.

To check the method of handling the solutions, bulbs were filled consecutively and analyzed. An example of the type of results obtained is given in Table. I. From this and similar experiments it was concluded that the method of handling the solutions was satisfactory.

TABLE I

Cell	ClO₂ titre	Cl₂	Total halogen
1	22.60	0.32	4.84
2	22.65	0.37	4.92

Experiments done during the latter part of this work indicated that Cl_2O, Cl_2O_6, and Cl_2O_7 are present in the decomposition mixture. Chlorine monoxide reacts with potassium iodide, Cl_2O_7 gives perchloric acid in water, and Cl_2O_6 may give chloric acid and perchloric acid. Thus the change in titre obtained by the potassium iodide-potassium iodate method outlined above does not represent the change in chlorine dioxide. A method was therefore devised whereby the chlorine and chlorine dioxide can be estimated apart from Cl_2O, Cl_2O_6, and Cl_2O_7. The method included the determination of these oxides from the products of their reaction with water.

The procedure adopted for complete analysis is as follows. By means of a siphon, the decomposition mixture is transferred quantitatively to a bottle containing 10 cc. of 0.1 N hydrochloric acid in 50 cc. of water. The stopcocks on the bottle are closed and the mixture is shaken vigorously, then kept in the dark until the mist has settled. Air is drawn through the bottle and through a series of three tubes containing a solution of potassium iodide.

The chlorine dioxide and chlorine carried off by the air are absorbed by the potassium iodide solution. Aspirating for one to one and one-half hours is sufficient to remove chlorine dioxide and chlorine. The amounts of chlorine dioxide and chlorine are determined by the usual titration of the potassium iodide solutions obtained.

The solution in the bottle now contains hydrochloric acid, chloric acid, and perchloric acid. The last two are formed in the reaction of Cl_2O_6 and Cl_2O_7 with water. The hypochlorous acid formed in the reaction of chlorine monoxide with water is removed by the foregoing treatment according to the reaction

$$HCl + HClO \rightleftarrows Cl_2 + H_2O \tag{4}$$

The amount of hydrochloric acid lost from the solution gives a measure of the hypochlorous acid that was present.

The carbon tetrachloride is separated from the water layer in a separatory funnel, and the water solution is neutralized with standard base, phenolphthalein being used as an indicator. The end point is quite stable in chloric acid and perchloric acid of the concentrations obtained here. The amount of base required gives the amount of $HCl + HClO_3 + HClO_4$ that was present. The neutralized solution is slightly acidified with sulphuric acid and the Cl^- precipitated with a solution of silver sulphate. The silver chloride is collected and weighed; the amount gives a measure of the hydrochloric acid that was left after the aspiratory process. Since the amount of hydrochloric acid added is known, the amount lost and thus the hypochlorous acid that was present can be calculated. Subtraction of the acid equivalent of the silver chloride from the acidity determined in the base titration gives the $HClO_3 + HClO_4$ that was present.

The excess Ag^+ in the filtrate from the chloride determination is precipitated with sodium chloride and the silver chloride filtered off. The solution is neutralized and evaporated to about 75 cc. The ClO_3^- is determined by the ferrous sulphate method, using $0.1\ N$ potassium permanganate to determine the excess Fe^{++} used. The perchloric acid can now be calculated by difference.

If the solution analyzed contains bromine, it is sometimes necessary to extract the water layer obtained from the carbon tetrachloride separation with a small amount of carbon tetrachloride. The bromine does not come over completely even after aspirating for one and one-half hours.

The following checks on this procedure have been applied.

Two samples of a solution of chlorine dioxide in carbon tetrachloride were weighed. One sample was analyzed directly by the potassium iodide-potassium iodate method. The following amounts of chlorine dioxide and chlorine were found: ClO_2, 2.67; Cl_2, 0.27. The other sample was treated exactly as outlined in the procedure for complete analysis. For the same weight of solution as above: ClO_2, 2.67; Cl_2, 0.16. Amount of hydrochloric acid added, 10.02 cc.; amount of hydrochloric acid found, 10.00 cc. No hypochlorous

acid, chloric acid, or perchloric acid was found.   A second experiment gave for direct titration: ClO_2, 8.10; Cl_2, 0.32.   For complete analysis: ClO_2, 8.08; Cl_2, 0.20.` Added 9.80 cc. HCl; found 9.79 cc. HCl.

These experiments show:

(1) That the method is quantitative for chlorine dioxide; none of the chlorine dioxide remains as oxyhalogen acids,

(2) That there is no appreciable loss of hydrochloric acid by entrainment or evaporation.

Experiments with chlorine monoxide in water showed that the removal of hypochlorous acid is complete if excess hydrochloric acid is present.   No oxidizing material remains after aspirating for one and one-half hours.   Mr. R. Ralston has shown by test runs in this laboratory, using chlorine monoxide many times (about ten) more concentrated, that only about 1% of chlorine monoxide comes over as the oxide, the rest reacting with water to give hypochlorous acid, which then reacts with hydrochloric acid according to Reaction (4).

Experiments with chloric acid (prepared from barium chlorate and sulphuric acid) and hydrochloric acid mixtures showed that at the concentrations obtained in our runs no oxidizing material is carried over in the aspiratory process.   A mixture subjected to the procedure outlined above gave an analysis for chloric acid agreeing to within 3% of what was added.

Finally, the ClO_4^- was determined by the titanous sulphate method (23) and good agreement with the value calculated by difference was obtained. For example, in one experiment: $ClO_4^- = 1.52 \times 10^{-4}$ moles, by titanous sulphate method; by difference, $ClO_4^- = 1.44 \times 10^{-4}$ moles.   In another experiment, $ClO_4^- = 2.96 \times 10^{-4}$, by reduction; by difference $= 2.99 \times 10^{-4}$ moles.   It was found necessary to boil for two and one-half to three hours to effect complete reduction of the ClO_4^- by Ti^{+++}.

As the amounts dealt with in the water extract are small, the percentage error in the determinations is quite high, usually about 5%.

In spite of the formation of considerable amounts of Cl_2O_6 and Cl_2O_7, the direct titration of the decomposition mixture during the early work did not show any significant discrepancies in the total halogen balance.   While this is at first surprising, consideration of a hypothetical case shows that the formation of relatively large amounts of Cl_2O_6 or Cl_2O_7 produces only small discrepancies in the halogen balance.

Experimental Results

Preliminary Experiments: Experiments on Thermal Decomposition

All results, except where otherwise stated, were obtained with carbon tetrachloride purified by the method described.

At 20° C. the thermal decomposition was particularly troublesome.   Experiments soon showed that if the solutions prepared were kept carefully shielded from light they would decompose only very slowly, in agreement with observations of Luther and Hoffmann (15).

In the first experiments the light was measured with the thermopile behind the cell and the incident intensity obtained by substituting a similar cell filled with carbon tetrachloride. The estimation of chlorine dioxide and chlorine was made by means of the direct potassium iodide-potassium iodate method.

It was found that solutions of chlorine dioxide in carefully purified carbon tetrachloride which have not been exposed to light are thermally stable, *e.g.*, no measurable decomposition takes place in six hours at 20° C. At the concentrations used, λ 5460 Å does not bring about any decomposition of chlorine dioxide (the absorption of this wave-length at the concentrations used is less than 0.5%), but on the addition of bromine, λ 5460 Å is absorbed and a sensitized reaction takes place. When the solution was insolated for 10 min. and then kept in the dark for three hours at 20° C., a large thermal reaction was initiated. In another experiment water was added to the solution in the cell. The mixture was insolated for 10 min. and then left in the dark for three hours at 20° C. No thermal change took place. In a further experiment, the solution was insolated for 10 min. and then kept for three hours at 3° C. Again there was no appreciable thermal decomposition. These experiments demonstrated that light initiates a thermal decomposition at 20° C. which does not, however, take place in wet carbon tetrachloride or at 3° C. With wet carbon tetrachloride, the solutions become cloudy on insolation; this makes accurate light measurements impossible.

The unsensitized reaction at 3650 Å shows the same effect, *i.e.*, a thermal reaction is initiated by 10 min. insolation at 20° C. but not at 3° C. The remainder of the work was therefore carried out at 3° C. where thermal decomposition is negligible.

Products of the Photodecomposition

Previous workers on the photodecomposition of chlorine dioxide in carbon tetrachloride solution have stated that chlorine and oxygen are the only products of the reaction. Bowen (5) examined insolated chlorine dioxide solutions analytically to determine whether Cl_2O_6 was formed, and he reported negative results.

Since Cl_2O_6 is formed in the gaseous photodecomposition of chlorine dioxide (2, 27, p. 269), it was thought worthwhile to look for evidence of it in the photo-reaction in solution. Accordingly, a solution of chlorine dioxide at 3° C. was strongly insolated with light of wave-length 3650 Å. The reaction mixture was forced into water and shaken up. A heavy mist was observed, identical in appearance with that which forms when Cl_2O_6 reacts with water. The chlorine dioxide and chlorine were removed from the water extract by aspirating air through for a period of three hours. The resulting solution had the odor of chlorine water but gave no precipitate with silver nitrate. It oxidized potassium iodide but did not reduce potassium permanganate. Thus ClO^- was indicated, and ClO_2^- and Cl^- were concluded to be absent. ClO^- was further confirmed since a small amount of solution decolorized indigo dissolved in concentrated sulphuric acid.

To test for ClO_3^- and ClO_4^-, a known amount of hydrochloric acid was added to the remainder of the water extract and the solution aspirated until no more oxidizing material passed over. This oxidizing substance was absorbed in potassium iodide and the amount determined. Thus, it was possible to calculate the hydrochloric acid which had reacted with the hypochlorous acid and came over as chlorine. The solution was now neutralized with standard potassium hydroxide. Acid in excess of the hydrochloric acid was observed to be present. This solution was evaporated to a small volume. Microscopic examination of the crystals obtained showed potassium chlorate and perchlorate. The presence of ClO_4^- was also demonstrated by the characteristic crystals obtained when a drop of 2% brucine solution was added to a drop of the test solution on a microscope slide. The outer part of the drop formed a brown ring, which is also characteristic of ClO_3^-. The tests were compared with similar tests on pure substances.

These qualitative tests showed that chloric acid, perchloric acid and hypochlorous acid were present in the water extract of the reaction mixture. By application of the method for complete analysis, quantitative estimation of the amounts was possible.

Table II shows the type of results obtained on carrying out the complete analysis.

Throughout this report the amounts of these acids found will be given in terms of the amount of 0.1 N acid they represent. This converts them to the same basis, as regards halogen, as the figures for chlorine dioxide.

TABLE II

COMPLETE ANALYSIS, HIGH LIGHT INTENSITY

Run No.	Amount ClO₂	Temp., °C.	Time, min.	ΔClO₂	HClO	HClO₃	HClO₄
1	18.54	3	240	13.82	1.64	0.66	2.34
2	8.14	3	60	3.74	0.75	0.41	0.55
3	14.51	3	60	4.00	1.02	0.55	0.54
4	17.43	20	60	4.33	0.89	0.20	0.60
5	21.18	3	240	6.14	1.48	0.71	1.48
6	10.66	3	25	6.08	1.29	0.52	· 1.16

In the experiments listed in Table II the HClO₃ + HClO₄ found represents about one-quarter of the total halogen of the chlorine dioxide which decomposed, while the hypochlorous acid represents about one-fifth. The table illustrates clearly the importance of using the complete analysis.

As possibilities to account for these acids in the water extract there are the oxides Cl_2O, Cl_2O_3, Cl_2O_6, and Cl_2O_7.

Cl_2O_3 (27, p. 269) is assumed to react with water to give two moles of chlorous acid which interact to give equal amounts of hypochlorous acid and

chloric acid. Since the presence of these acids is observed, it might be supposed that Cl_2O_3 was present. This oxide, however, requires equal amounts of hypochlorous acid and chloric acid; *i.e.*, chloric acid in excess of hypochlorous, if Cl_2O_6 is present. In all our experiments the chloric acid is less than the hypochlorous acid. Hence, it is concluded that the formation of the oxyhalogen acids found is better explained by the presence of other oxides.

The hypochlorous acid can readily be explained by the presence in the decomposition mixture of chlorine monoxide which reacts with water to give this acid.

The $HClO_3 + HClO_4$ can be explained by the reaction of Cl_2O_6 with water. Experiments have shown that when Cl_2O_6 reacts with water, chloric acid and perchloric acid are formed; perchloric acid always being in excess of the chloric acid. This relation was accounted for by the decomposition in the reaction zone of chloric acid to perchloric acid and ClO_2, by means of the strongly dehydrating Cl_2O_6. However, when, as in our experiments on the decomposition of chlorine dioxide, there is a dilute solution of Cl_2O_6 in carbon tetrachloride, this mode of action would not apply, and the Cl_2O_6 would be expected to yield equal quantities of chloric acid and perchloric acid. This possibility was tested by preparing a dilute solution of Cl_2O_6 in carbon tetrachloride by bubbling ozone through a cold solution of chlorine dioxide in carbon tetrachloride. The resulting solution was treated as in the procedure for complete analysis. Found: $HClO_3$, 0.22; $HClO_4$, 0.24. This experiment demonstrated that Cl_2O_6 acts under our conditions as the mixed anhydride of chloric acid and perchloric acid. Additional support is lent to this by the fact that in some experiments (Table II, Experiments 2 and 3) using high concentrations of chlorine dioxide and small fractional decomposition, the ClO_3^- is very nearly equal to the ClO_4^-. This is what would be expected if Cl_2O_6 were formed and if none of it were decomposed to Cl_2O_7.

Thus, it can reasonably be assumed that the chloric acid represents the Cl_2O_6 present. The perchloric acid in excess of chloric acid can be assumed to be formed from Cl_2O_7. This oxide is formed on continued insolation of gaseous chlorine dioxide (3). It would be expected that the solution in carbon tetrachloride would show similar behavior.

Of these oxides, Cl_2O and Cl_2O_6 undergo further decomposition. Experiments 1, 2, and 3 in Table IX indicate that the amount of ClO_3^- increases from zero, at the beginning, to a maximum. An experiment was performed in which a solution of chlorine dioxide was insolated with 3650 Å. The absorption of green light by this solution was determined at intervals during the decomposition.

Experiment 1 N (*N* will be used to characterize all experiments not tabulated.)

ClO₂ initial, 14.60				ClO₂ final, 0.31			ΔClO₂, 14.29		
Time, min.	0	30	45	60	75	90	120	180	255	315
Per cent absorption for 5460 Å	0.2	3.0	3.5	3.7	3.4	4.4	2.1	2.2	1.4	0.3

The absorption rises to a maximum, then falls off. The amount of ClO_3^- formed during a decomposition shows the same behavior. Cl_2O_6 would be expected to absorb 5460 Å strongly (11), and it may reasonably be assumed that the change in absorption is due to this oxide. The absorption coefficient of gaseous chlorine monoxide for 5460 Å is about 0.00003 (9) in terms of millimetres of pressure and centimetres of absorbing path. Chlorine monoxide equivalent to 2 cc. of 0.1 N hypochlorous acid per cell would give an absorption of only 0.5%. This is about the maximum amount of chlorine monoxide ever obtained, which cannot therefore explain the above absorption.

The value of the extinction coefficient of Cl_2O_6 in carbon tetrachloride solution for λ 5460 Å is not known. Goodeve and Richardson give values for the extinction coefficient of liquid Cl_2O_6 up to the wave-length 5700 Å. The coefficient increases rapidly up to this point, where a value of 63 (moles per litre, centimetres of absorbing path) is reached. If a value of 100 for the extinction coefficient at 5460 Å is assumed, calculation shows that Cl_2O_6 equivalent to 0.5 cc. of chloric acid in the cell would show an absorption of 50% for green light. The maximum absorption observed is about 4%. On the assumption of an absorption coefficient of 10 for Cl_2O_6, the absorption would be about 6% for the amount represented by 0.5 cc. of chloric acid. Since the extinction coefficient may increase or decrease with decreasing wave-length, the above evidence is inconclusive, but is quite compatible with the presence of Cl_2O_6. The facts that Cl_2O_6 is formed in the gaseous decomposition and that in the experiments with low percentage decomposition $HClO_3$ and $HClO_4$ are formed in equal amount still incline the authors to the conclusion that Cl_2O_6 is present.

Experiment 1 N, which was carried out to complete decomposition, yielded at the end of the run no chloric acid and no hypochlorous acid, but 2.99 cc. of 0.1 N perchloric acid. This value was checked by means of the titanous sulphate reduction. Thus it appears that the Cl_2O and Cl_2O_6 are themselves decomposed and only Cl_2, O_2, and Cl_2O_7 are obtained as end products. Cl_2O_7 does not absorb 3650 Å (12) and appears to be quite stable. About one-fifth of the chlorine dioxide decomposed went to form this oxide.

Experiments conducted at 20° and 30° C. give analyses similar to the above, except that the chloric acid is much less, or even absent. This behavior would be expected of Cl_2O_6; it might equally well apply to Cl_2O_3.

Experiment 2N: 30° C., intense beam, complete analysis. ClO_2 initial, 12.61; ΔClO_2, 10.79; $HClO$, 0.77; $HClO_4$, 2.27; $HClO_3$, 0.00.

Experiment 3N: 20° C., intense beam, complete analysis. ClO_2 initial, 19.87; ΔClO_2, 10.89; time, 1.5 hr. $HClO$, 1.91; $HClO_3$, 0.20; $HClO_4$, 2.15.

Experiment 4N: 3° C. This is added for comparison with 3N. It was done with the same light beam. ClO_2 initial, 27.36; ΔClO_2, 11.45; $HClO$, 2.25; $HClO_3$, 1.14; $HClO_4$, 1.87.

Comparison of Experiments 3N and 4N shows that whereas the amount of chloric acid is much less at 20° C. than at 3° C., that of hypochlorous acid

shows little difference at the two temperatures. It appears that at 30° C. the Cl_2O_6 is decomposed as rapidly as it is formed; at 20 °C. it is also decomposed rapidly.

Decomposition with the wave-length 4360 Å yields reaction products of the same kind in about the same relative amounts as are obtained with 3650 Å. (See Experiment 8N.)

The results of complete analyses on decomposition mixtures from the bromine sensitized reaction with wave-length 5460 Å are given in Table III.

TABLE III

BROMINE SENSITIZED DECOMPOSITION OF CHLORINE DIOXIDE SOLUTIONS (λ 5460 Å), COMPLETE ANALYSIS

Run No.	Amount ClO_2	Temp., °C.	Time, min.	Decomp. ClO_2	ClO^-	ClO_3^-	ClO_4^-
1	20.50	3	180	3.74	0.34	0.30	0.64
2	10.00	3	180	2.91	.20	.35	.67
3	10.16	3	180	1.63	.30	.23	.37
4	9.32	3	250	3.92	.03	.11	.68

In the bromine sensitized decomposition, the chloric acid and perchloric acid represent about one-fifth of the total halogen of the chlorine dioxide decomposed. The amounts of hypochlorous acid found, though small, appear to be definite. In Experiment 4 the bromine content was very high (85% abs.). The results show that the amount of Cl_2O_6 is less in this experiment than in the others and may mean that Cl_2O_6 undergoes a bromine sensitized decomposition. Experiments by Mr. Ralston in this laboratory have shown that chlorine monoxide undergoes a bromine sensitized decomposition, and consequently only small amounts of this oxide would be able to accumulate.

Measurement of the Quantum Yield

The experiments on the thermal decomposition showed that it would be necessary to conduct the work at about 3° C. For the measurements in Table IV a small bath, well insulated and of sufficient size to accommodate the thermopile and cell, was constructed. The ice was contained in cans; this kept the water optically clear. The thermopile was placed as close to the cell as possible. A light beam, the same as that used in the early quantum yield experiments, but of greater cross section, was used.

TABLE IV

COMPLETE ANALYSIS, 3° C.

Exp. No.	Amount ClO_2	ΔClO_2	Time, min.	Amount light absorbed, mm.	
1	6.57	2.88	480	140	2.04
2	11.87	2.81	420	143	2.23

Scattered light was estimated by settings of the thermopile. The amount was about 10% of the total.

To check these values, a measurement of the quantum yield of the uranyl oxalate decomposition was made. The value for this reaction is accurately known and the procedure has been described in detail (28). No departure was made from the procedure outlined there. The oxalic acid concentration used was about 0.1 M. The solutions were stirred continuously. Using the same beam and applying the correction for scattering, we obtained a value of 0.55 for γ. The accepted value is 0.492. Correcting our values for γ_{3650} by multiplying by the ratio $\dfrac{0.492}{0.55}$, values of 1.83 and 1.99 for Experiments 1 and 2 respectively are obtained. Better agreement in the values need not be expected. The values obtained agree with those of Nagai and Goodeve ($\gamma = 1.98$) and Bowen and Cheung ($\gamma = 2.00$).

To determine whether there is a large difference in the decomposition for the same amount of light absorbed at 3° and at 20° C., the experiments listed in Table V were performed.

TABLE V

HIGH INTENSITY, DIRECT ANALYSIS

Series	Run No.	Amount ClO₂	Temp., °C.	Time, min.	ΔClO₂	Ratio
1	1	2.09	19.5	45	0.788	1.263
	2	1.92	3.5	45	0.624	
2	1	3.78	19.5	45	2.904	1.172
	2	3.63	3.5	45	2.482	

Series 2 was done with a light intensity about four times as great as that in Series 1. These experiments show that probably the only difference in the reaction at the two temperatures is that at 20° C. the photodecomposition is accompanied by a thermal reaction. At the light intensity used, this is slow compared to the light reaction.

An experiment was performed in which the set-up for the intense beam was used. The decomposition of a chlorine dioxide solution exposed for a definite time was determined by the method for complete analysis. Then a solution of uranyl oxalate was exposed for a certain length of time with the same optical set-up. The absorption of the solution was measured, and assuming the same quantum yield for the uranyl oxalate decomposition at the high intensity as at the low, we could calculate the quantum yield of the reaction with λ 3650 Å. An experiment on the bromine sensitized decomposition was done at the same time to compare γ_{3650} with γ_{5460}. The experiments and results are reported below.

Experiment 5N. Decomposition of chlorine dioxide with λ3650 Å; complete analysis; 3° C.; high intensity beam; time, 64 min. ClO₂ initial, 13.40; ΔClO₂, 12.53; % abs. = 96 (for comparison with uranyl oxalate experiment). Rel. $I_{abs.}$ = 212 (for comparison with bromine sensitized decomposition).

Experiment 6N. Decomposition of uranyl oxalate with λ 3650 Å; beam as above; 22° C.; time, 64 min.; change in oxalic acid is equivalent to 13.13 cc. 0.04896 N potassium permanganate. % abs. of solution, 44.4; γ_{3650} calculated from this data = 2.15. The agreement with the results obtained with the small beam is fairly good.

Experiment 7N. Bromine sensitized decomposition of chlorine dioxide by λ 5460 Å: 3° C.; beam as above; time, 64 min. ClO_2 initial, 12.42; ΔClO_2, 1.77; Rel. $I_{abs.}$, 185; % abs., 80; $\dfrac{\gamma_{3650}}{\gamma_{5460}} = 9.23$.

This experiment places the quantum yield for the bromine sensitized reaction with high bromine concentration at $\dfrac{2.15}{9.23} = 0.233$.

Another experiment was performed in which the quantum yields at 3650 Å and at 5460 Å were compared (Table VI).

TABLE VI

DIRECT ANALYSIS, HIGH INTENSITY

Exp. No.	Amount ClO_2	Temp., °C.	λ, Å	Rel. no. quanta abs.	Decomposition	Relative γ
1	13.20	3	3650	4.149	7.94	7.50
2	13.20	3	5460	3.684	0.94	1.00

The absorption of the bromine sensitized solution was about 45%. This experiment places γ for a solution with a moderate concentration of bromine at $\dfrac{2.00}{7.50} = 0.27$.

Further values of γ for the sensitized decomposition of chlorine dioxide solutions, using λ 5460 Å, are given in Table VII. Experiments reported later will show that there is a real variation in the values of γ for the bromine sensitized decomposition.

A comparison of γ_{3650} with γ_{4360} was also made.

TABLE VII

DIRECT ANALYSIS. QUANTUM YIELDS FOR THE BROMINE SENSITIZED REACTION (λ 5460 Å)

Initial ClO_2	Per cent light absorbed (by Br_2)	γ
1.934	48.7	.22
6.104	47.0	.28
6.008	48.0	.32
1.732	14.6	.28
1.560	72.0	.19
6.788	77.3	.22

Experiment 8N: Temp., 3° C., high light intensity, complete analysis. $\dfrac{I_{abs.}\,3650}{I_{abs.}\,4360} = 1.31$. With 3650 Å: ClO_2 initial, 9.63; ΔClO_2, 4.30; time, 40 min. ClO^-, 0.89; ClO_3^-, 0.25; ClO_4^-. 0.75.

With 4360 Å: ClO_2 initial, 9.61; ΔClO_2, 3.19; time, 60 min. ClO^-, 0.66; ClO_3^-, 0.33; ClO_4^-, 0.49. $\dfrac{\gamma_{3650}}{\gamma_{4360}} = 1.86$.

This experiment places the quantum yield of the decomposition with λ 4360 Å at about 1. This value is in agreement with the published value (6).

To sum up, on the basis of this work the quantum yield of the unsensitized decomposition with 3650 Å is 2.0;, with 4360 Å, 1.0; and that of the bromine sensitized decomposition with 5460 Å is 0.2 to 0.3.

EXPERIMENTS ON THE KINETICS OF THE UNSENSITIZED DECOMPOSITION WITH $\lambda = 3650$ Å

Effect of Concentration of Chlorine Dioxide

These experiments show that increasing the concentration increases the amount of decomposition per unit of light absorbed (compare Table XII).

TABLE VIII

HIGH INTENSITY, $I_{abs.}$ SAME IN EACH CASE, COMPLETE ANALYSIS

Run No.	Amount ClO₂	Amount ClO₂ de- composed	Time, min.	Temp., °C.	HClO	HClO₃	HClO₄
1	4.82	4.29	45	3	0.34	0.00	0.70
2	14.65	5.87	45	3	1.09	.59	.77
3	21.94	6.62	45	3	1.27	.77	.81

Variation of Decomposition with Time

It can be seen from Table IX that the rate falls off with time. During the first 45 min. period the decomposition is 6.62, during the next period it is 4.83, and during the third it is 3.80.

TABLE IX

Run No.	Amount ClO₂	Amount ClO₂ de- composed	Time, min.	Temp., °C.	HClO	HClO₃	HClO₄
1	21.94	6.62	45	3	1.27	0.77	0.81
2	27.36	11.45	90	3	2.25	1.14	1.87
3	22.50	15.25	135	3	2.04	0.88	2.72

NOTE:—*Except for time, conditions as above.*

Variation of Decomposition with Light Intensity

The change in light intensity was effected by interposing a screen of 36% transmission.

TABLE X

COMPLETE ANALYSIS

Run No.	Amount ClO₂	Amount ClO₂ de- composed	Time, min.	Rel. $I_{abs.}$	HClO	HClO₃	HClO₄
1	27.36	11.45	90	100	2.25	1.14	1.87
2	21.30	4.50	90	36	1.08	0.44	0.72

NOTE:—*Light beam as above.*

If the decomposition were proportional to $I_{abs.}$, decomposition in Experiment 1 should have been 12.50.

Formation of Chlorine Monoxide

An experiment was performed to determine whether chlorine monoxide is formed by the reaction

$$Cl_2 + ClO \longrightarrow Cl_2O + Cl \ (-14 \ Cal.)$$

Though the reaction is endothermic (about -14 Cal.) reactants with sufficient energy might give chlorine monoxide and chlorine.

Two samples of chlorine dioxide were used; to one, excess chlorine was added. If the reaction above competes with another reaction of the ClO groups (*e.g.*, $ClO + ClO \longrightarrow Cl_2 + O_2$), increasing the concentration of chlorine should increase the rate of this reaction, and a greater amount of chlorine monoxide should be formed in this case.

TABLE XI

HIGH INTENSITY, COMPLETE ANALYSIS

Run No.	Amount ClO_2	Time, min.	Initial Cl_2	ΔClO_2	Final Cl_2	HClO	$HClO_3 + HClO_4$
1	8.96	95	6.25	7.86	12.80	0.58	1.41
2	8.92	95	.94	6.95	5.80	0.53	1.22

This experiment shows that within the accuracy of the analysis there is no difference in the amounts of chlorine monoxide in each run. In Experiment 1 there was greater photolysis. This may account for the slightly greater amounts of ClO^- and $HClO_3 + HClO_4$.

Experiments on Stirring

Chlorine dioxide absorbs λ 3650 Å very strongly and, therefore, in the absence of stirring, marked concentration differences are set up during photolysis. It was thus expected that stirring the solutions would alter the rate of decomposition.

TABLE XII

Run No.	Description	Initial ClO_2	Time, min.	ΔClO_2	HClO	$HClO_3$	$HClO_4$
1	Unstirred	24.26	30	10.52	1.97	1.29	2.12
2	Stirred	24.06	30	11.60	1.91	1.14	1.94
3	Stirred	15.34	30	11.36	1.18	0.56	2.16

Table XII shows that the photolysis is about 10% greater in a stirred solution. Experiment 3, done with a stirred solution at lower concentration, shows that stirring markedly decreases the effect of concentration on the rate of decomposition. The effect of variation of light intensity may also be negligible in stirred solutions, though this was not tested.

KINETICS OF THE PHOTODECOMPOSITION WITH λ 4360 Å

Effect of Concentration on Rate of Decomposition

Experiments, similar to those reported above for λ 3650 Å, were carried out with λ 4360 Å. They gave analogous results, *i.e.*, the rate of decomposition in unstirred solutions increases slightly with increasing concentration of chlorine dioxide but decreases with time. They will not be reported further here.

KINETICS OF THE BROMINE SENSITIZED DECOMPOSITION WITH λ 5460 Å

The Influence of Concentration of Chlorine Dioxide

The results of this study are given in Table XIII. Comparisons are to be made only between values within any series, where the only factor varied is the chlorine dioxide concentration. Concentration of bromine, light intensity, and the period of illumination vary from series to series.

TABLE XIII
DIRECT ANALYSIS

Series	Exp. No.	Initial ClO₂	Per cent absorbed by Br₂	Time, min.	ΔClO₂
1	1	5.71	41	90	0.284
	2	1.71	41	90	.240
2	1	1.22	40	60	.404
	2	2.24	40	60	.389
	3	3.79	40	60	.424
	4	5.35	40	60	.456
	5	8.09	40	60	.396
3	1	12.58	53	60	.532
	2	4.91	53	60	.526
4	1	9.64	71	60	.408
	2	3.71	71	60	.364
	3	1.85	71	60	.440
5 .	1	0.53	65	45	.438
	2	3.28	65	45	.504
	3	8.35	65	45	.542
6	1	1.26	32	60	.552
	2	3.95	32	60	.632
	3	9.07	32		
7	1	4.65		60	.002
	2	8.48		60	.009

Series 1–4 were done with U.S.P. carbon tetrachloride purified by the method outlined. Series 5–7 were done with c.p. carbon tetrachloride treated in the same way. In Series 7 no bromine was added, so this gives the unsensitized decomposition of the chlorine dioxide by green light. If these values are subtracted (for corresponding concentrations) from those for the sensitized decomposition, there appears to be no significant variation of the decomposition per unit time with chlorine dioxide concentration.

The non-variation of rate of decomposition with chlorine dioxide concentration has also been checked by the procedure for complete analysis.

TABLE XIV

Exp. No.	Initial ClO_2	Mean ClO_2	Time, min.	ΔClO_2	HClO	$HClO_3$	$HClO_4$
1	9.47	8.08	210	2.77	0.16	0.20	0.54
2	6.25	4.96	210	2.58	−0.01	0.16	0.38

The variation of rate of decomposition with almost twofold change in chlorine dioxide is slight.

Variation of Concentration of Bromine

The results of this study are given in Table XV. Within any series, the only factor varied was the bromine concentration. This quantity is given in terms of the percentage absorption, to which it is related by the expression

$$\log \frac{I}{I_0} = -\alpha cd; \frac{I}{I_0} = \text{fraction of light transmitted.}$$

TABLE XV

Series	Exp. No.	Initial conc. ClO_2	Per cent absorbed	Time, min.	ΔClO_2	Compare decomp. $\propto I$
1	1	1.57	40.0	60	0.566	1.086
	2	1.57	76.7	60	.952	
2	1	1.74	52.0	75	.450	0.756
	2	1.74	87.3	75	.646	
3	1	1.19	21.7	70	.376	0.908
	2	0.81	52.3	70	.750	

Column 7 gives values calculated from the decomposition with low absorption, on the assumption of a direct proportionality between percentage absorption and rate of decomposition. They are to be compared with the values opposite them in the adjacent column. There is apparently a departure from a linear relation.

Variation of Rate of Decomposition with Light Intensity

The light intensity was varied by interposing screens of the transmission indicated.

It appears that the decomposition does not vary directly as the intensity of the light. In Column 8, Table XVI, values calculated from the decomposition at low intensity are compared, on the assumption of a $\sqrt{I}$ relation. The values calculated on this basis are near, but always below, the values observed.

TABLE XVI

Series	Exp. No.	Initial conc. ClO_2	Relative intensity	Per cent absorption	Time, min.	Decom-position	Compare $\propto \sqrt{I}$
1	1	1.74	36	52.0	90	0.200	
	2	1.74	100	52.0	90	.403	0.332
2	1	1.57	36	65.1 .	90	.532	
	2	1.57	100	65.1	90	.908	.852
3	1	3.43	36	58.8	60	.228	
	2	3.43	100	58.8	60	.428	.380
4	1	1.13	36	52	70	.394	
	2	1.12	100	52	100	.704	.658
	3	1.13	100		100	.008	
5	1	3.42	51.3	54	60	.466	
	2	3.41	100	54	60	.686	.552
	3	4.58	100		60	.004	
6	1	6.97	100	60	46	1.132	1.00
	2	6.93	36	60	46	0.600	

These results were also checked by doing experiments in which the procedure for complete analysis was used.

TABLE XVII

Series	Exp. No.	Initial ClO_2	Relative intensity	Time, min.	ΔClO_2	Compare $\propto I$	$HClO$	$HClO_3$	$HClO_4$
1	1	2.95	100	180	2.91	4.53	.34	.31	.67
	2	2.98	36	180	1.63		.20	.35	.67
2	. 1	7.80	36	230	0.82		.30	.23	.37
	2	7.84	100	230	1.96	2.28			

This table also demonstrates that the rate of decomposition does not vary directly as the amount of light absorbed. Greater absorption means relatively less decomposition.

It was considered worthwhile to test whether stirring the solution would alter the rate of decomposition. Parallel runs were made, one solution being stirred, the other being left undisturbed.

It was concluded that stirring makes no difference to the kinetics of the bromine sensitized decomposition.

TABLE XVIII
COMPLETE ANALYSIS, 68% ABSORPTION

Run No.	Description	Initial ClO_2	Time, min.	ΔClO_2
1	Unstirred	5.86	225	1.550
2	Stirred	5.97 .	225	1.536

Experiments on Bromine Chloride Formation

Papers have appeared in the literature (1, 13, 29) showing that bromine chloride is formed in mixtures of bromine and chlorine in the gas phase and in carbon tetrachloride solution. Since in our experiments chlorine results from the decomposition of chlorine dioxide, it seemed desirable to ascertain whether bromine chloride was formed here.

The amount of bromine chloride formation can be estimated from the change in absorption of the solution for the line 5460 Å. Bromine chloride absorbs this line weakly, whereas bromine shows a strong absorption. ($\alpha_{BrCl}/\alpha_{Br_2} = 0.0405$.) A decrease in absorption should be noticed if bromine chloride is formed.

Some experiments were done with bromine and chlorine mixtures alone in carbon tetrachloride.

Experiment 9N: Br$_2$ concentration, 2.026; Cl$_2$ concentration, 2.010. Five minutes after mixing (at room temperature before exposure to light) the free bromine concentration dropped to 1.95, and further change was very slow. On insolating with the full light of the mercury lamp for seven minutes, bromine dropped to 1.025. Further insolation produced no change.

Experiment 10N: Bromine (conc. 2.089) and chlorine (conc. 2.130) were mixed and insolated with green light at 3° C. for two hours. During this time the concentration of bromine dropped to 1.070.

Experiment 11N: The cell contained Cl$_2$, 2.21; Br$_2$, 1.3; ClO$_2$, 1.574. According to a graph experimentally determined, bromine of this concentration should give an absorption of 21.8%; the absorption measured was 22.2%.

Examination of a large number of experiments, of which the above are typical examples, indicates that, whereas bromine chloride is formed in bromine and chlorine mixtures alone, no formation of this compound could be detected under the conditions of these experiments with chlorine dioxide present.

Discussion of Results

Unsensitized Reaction

The unsensitized decomposition with λ 3650 Å will be discussed first, since the primary process following light absorption is known. The reaction mechanism must account for (1) the initiation of the thermal decomposition, (2) the formation of Cl$_2$O, Cl$_2$O$_6$, and Cl$_2$O$_7$ as well as chlorine and oxygen, (3) the quantum yield of 2, (4) the observed small variation of rate of decomposition with time, concentration of chlorine dioxide and light intensity in unstirred solutions, and non-variation with concentration in stirred solutions.

As stated in the Introduction, absorption of 3650 Å by gaseous chlorine dioxide produces ClO + O. The absorption spectrum of chlorine dioxide in solution appears to resemble in main outline that in the gas phase (16).

Therefore, for the unsensitized reaction at 3650 Å, in solution, we suppose

$$ClO_2 + h\nu \longrightarrow ClO + O \tag{5}$$

On the assumption that one quantum of light can dissociate one chlorine dioxide molecule, the quantum yield of approximately 2 can be explained by the occurrence of two further reactions:

$$ClO_2 + O + M \longrightarrow ClO_3 + M \tag{6}$$

$$ClO + ClO_2 \longrightarrow Cl_2O + O_2 \quad (+ 41.5 \text{ Cal.}) \tag{7}$$
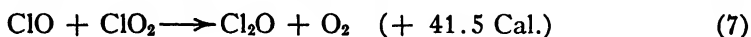
In the gas phase, a third body is assumed to be necessary to stabilize the collision in Reaction (6). In solution, three-body collisions will be much more numerous, and the reaction may thus be reasonably supposed to take place.

Since only about 10% of the chlorine dioxide decomposed appears as chlorine monoxide, ClO must also disappear by the reaction

$$ClO + ClO \longrightarrow Cl_2 + O_2 . \tag{8}$$
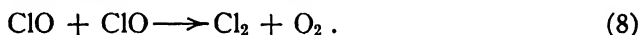
This reaction is supposed to have a low activation energy (25) and should thus occur quite readily, probably more readily than Reaction (7).

Actually, if the rate of disappearance of ClO by Reaction (7) is about the same as that by Reaction (8), the expression for the disappearance of chlorine dioxide is:

$$\frac{-d(ClO_2)}{dt} = k_1 I_{abs.} + k\sqrt{I_{abs.}} (ClO_2)$$

A marked variation with chlorine dioxide concentration and a non-linear variation with light intensity would be expected. Actually, in stirred solutions, the decomposition appears to be independent of chlorine dioxide concentration, and even in unstirred solutions the rate is almost directly proportional to the light intensity.

It is interesting to note that the assumption that Reaction (8) is relatively fast compared to Reaction (7) leads to an expression for the rate of formation of chlorine monoxide.

$$\frac{d\,Cl_2O}{dt} = k\sqrt{I_{abs.}} (ClO_2)$$

Experiments 1 and 2, Table X, indicate that the formation of chlorine monoxide approaches a $\sqrt{I}$ relation. (In Experiment 1, HClO = 3.15 would have been expected for direct proportionality, HClO = 1.80 for a $\sqrt{I}$ relation.) Reaction (7) provides a mechanism for the formation of chlorine monoxide. The scheme of Luther and Hoffmann (15) can then be used to explain the thermal decomposition initiated by a short insolation at 20° C. The inhibitory effect of water may be attributed to its reaction with chlorine monoxide.

The importance of Reaction (7) is rather difficult to estimate. The value of the molar extinction coefficient for chlorine monoxide at this wave-length, calculated from the value for the gas, is 0.458; that of chlorine dioxide is 1130. Therefore, little decomposition of chlorine monoxide by light absorp-

tion would be expected. Furthermore, experiments have been done which show that chlorine monoxide does not react thermally at an appreciable rate with chlorine dioxide at 3° C.

However, examination of Table IX on the variation of the decomposition with time, shows that at the end of $1\frac{1}{2}$ hr. the chlorine monoxide (represented by hypochlorous acid) is not quite twice that at the end of $\frac{3}{4}$ hr., and at $2\frac{1}{4}$ hr. the amount present has fallen off below the value at $1\frac{1}{2}$ hr. To account for this, a reaction of ClO with Cl_2O can be assumed.

$$ClO + Cl_2O \longrightarrow ClO_2 + Cl_2 \quad (+ 30 \text{ Cal.}) \tag{9}$$

Such a reaction will also account in part for the falling-off of the chlorine dioxide decomposition towards the end, since in this reaction chlorine dioxide is built up again. The formation of chlorine dioxide in the photodecomposition of chlorine monoxide makes Reaction (9) quite probable. Chlorine monoxide could also be removed by a chlorine sensitized photodecomposition.

Oxygen atoms combine as is shown by Reaction (6) and also by the reaction

$$O + O + M \longrightarrow O_2 + M \tag{10}$$

If Reaction (6) is fast relative to Reaction (10), independence of γ from (ClO_2) and light intensity will result.

Cl_2O_6 is formed by polymerization of the ClO_3 groups.

$$2ClO_3 \longrightarrow Cl_2O_6 \tag{11}$$

The fact that more Cl_2O_6 is not observed may be due to a number of causes. Cl_2O_6 shows increasingly high absorption towards the blue (11) and decomposes photochemically. Secondary reactions such as

$$Cl_2O_6 + O \longrightarrow Cl_2O_7 \tag{12}$$

would also tend to prevent the accumulation of Cl_2O_6. The fact that about one-fifth of the chlorine dioxide decomposed goes to the formation of Cl_2O_7 shows that a considerable amount of Cl_2O_6 must have been present.

The reaction with λ 4360 Å appears to be explicable by a similar mechanism.

Since the relative amounts of Cl_2O, Cl_2O_6, and Cl_2O_7 are about the same as with λ 3650 Å, it must be expected that similar groups would be formed in the primary light process.

The wave-length 4360 Å is just at the limit of the region where dissociation to ClO+O is energetically possible. However, a complex molecule in an electronically excited state may be able to make up the required energy in one of the normal vibrations by fluctuations in the energies of the other normal modes of vibration. A molecule of chlorine dioxide absorbing light may thus have a certain probability of dissociating even at a wave-length longer than the limit at which the quantum itself has sufficient energy for dissociation (10). The lower quantum yield can be ascribed to the lower efficiency of the primary light process at this wave-length.

The production of an excited molecule by the process

$$ClO_2 + h\nu \longrightarrow ClO_2^*$$

followed by

$$ClO_2^* + ClO_2 \longrightarrow ClO + ClO_3$$
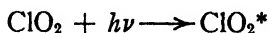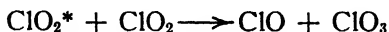
will also fit the facts qualitatively. No difference in the relative amounts of products by this process from those at λ 3650 Å would be expected on the basis of the mechanism proposed, and the lower quantum yield could be ascribed to deactivation of the ClO_2^*. However, unless we suppose that a constant fraction of the ClO_2^* reacts with chlorine dioxide, the reaction velocity will depend to a marked extent on (ClO_2). Thus a splitting into $ClO + O$ at 4360 Å is probable.

Sensitized Reaction

We proceed now to a discussion of the bromine sensitized decomposition of chlorine dioxide by λ 5460 Å.

A satisfactory theory should account for the following facts:

(1) The quantum yield of the decomposition is 0.2 to 0.3.

(2) The quantum yield does not vary with the chlorine dioxide concentration.

(3) There is a decrease in quantum yield with increasing light intensity and with increased bromine concentration. The variation of rate of decomposition with light intensity approaches a $\sqrt{I}$ relation.

(4) Large amounts of Cl_2O_6 and some chlorine monoxide appear to be formed.

In the sensitized decomposition, the light is absorbed by the bromine, and eventually brings about a decomposition of the chlorine dioxide.

The spectrum of bromine in the gas phase shows a convergence limit at 5107 Å. Beyond this there is a continuous absorption region which corresponds to a dissociation of the bromine molecule The products of the primary dissociation by light absorption in the continuum are one excited and one normal atom. Thus the convergence limit corresponds to the energy that is just sufficient to cause this dissociation. The excitation energy of the excited bromine atom is 0.431 volts. From this the energy corresponding to a dissociation to two normal atoms can be calculated. This energy corresponds to 6250 Å.

The discrete absorption of bromine extends from 6720 Å to the convergence limit. In the region between 6250 Å and the convergence limit, the primary product of light absorption is an excited molecule which has sufficient energy to dissociate to normal atoms if a suitable mechanism is provided; for example, collision with another molecule. There is, however, the possibility that absorption of green light produces bromine atoms directly, since there is a weak continuum underlying the discrete band system.

For bromine in carbon tetrachloride the absorption extends over the same range as for the gas, from 6720 Å to the ultra-violet. The spectrum is continuous throughout the whole region, but the shape of the absorption curve is the same as for the gas (18).

Rabinowitch and Wood have concluded from the behavior of strongly illuminated iodine solutions (19) that iodine dissociates with a quantum yield of 1, even in the discrete region of the spectrum, if the energy of the excited molecule is sufficient for dissociation to two normal atoms.

Thus, at the wave-length 5460 Å there is the possibility of the excited bromine dissociating to atoms either directly or on collision with carbon tetrachloride molecules. Wachholtz (30) from a study of the bromine and ethyl maleate reaction, and Schmidt (24) from a study of the bromine and methyl fumurate reaction (both reactions in carbon tetrachloride solution), concluded that the wave-length 5570 Å can produce dissociation to two atoms.

Let us consider the consequences of assuming an atomic process for the bromine sensitized decomposition of chlorine dioxide.

Rabinowitch and Wood (21) have suggested that collisions between particles in solution occur in sets. Two particles once brought together will suffer several consecutive collisions before they are separated. Consider a bromine molecule absorbing a quantum of wave-length 5460 Å. On our assumption, the excited bromine molecule will dissociate when it collides with a solvent molecule. But the two bromine atoms resulting are surrounded by heavy solvent molecules. Before they can separate completely, they may collide again. Since in solution every collision is a three-body collision, this will result in a recombination of the bromine atoms, the solvent molecule and bromine molecule sharing the energy liberated. If, for the conditions existing, n is the average number of consecutive collisions suffered by two inert particles, the probability of the bromine atoms separating before colliding is $1/n$, and therefore the probability of dissociation being fruitful is $1/n$. Thus the average yield of bromine atoms on the absorption of a quantum would be less than 2. The value of the quantum yield would depend on n, and would be $1/n$ of that obtained in the absence of the solvent.

The assumption of bromine atoms bringing about the decomposition of chlorine dioxide would thus explain the low quantum yield of the process; that is, the low yield would be attributed to the high probability of primary recombination.

Setting up equations for the process, we have:

$Br_2 + h\nu \longrightarrow 2Br$ (only $1/n$ of the quanta will bring about dissociation)

$Br + ClO_2 \longrightarrow$?

$Br + Br \longrightarrow Br_2$
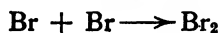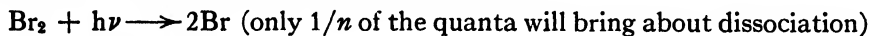
However, it is difficult to provide a mechanism for the reaction products which are observed. The reaction

$$Br + ClO_2 \longrightarrow BrCl + O_2,$$
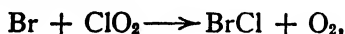
though certainly exothermic (47.2 Cal.), yields no groups which can give rise to Cl_2O_6 or Cl_2O. The reaction

$$Br + ClO_2 \longrightarrow BrO + ClO$$
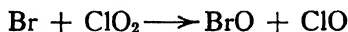
is also unsatisfactory; no reference to bromine oxide has been observed in the literature. An atomic process has therefore to be discarded for want of a plausible mechanism. The other possibility is that absorption of light produces an excited bromine molecule which transfers its energy to a chlorine dioxide molecule by collision.

Hence, the mechanism for the reaction is the same as that proposed for the corresponding gas reaction (27, p. 269).

$$Br_2 + h\nu \longrightarrow Br_2^*$$

$$Br_2^* + ClO_2 \longrightarrow ClO_2^* + Br_2$$

$$ClO_2^* + ClO_2 \longrightarrow ClO_3 + ClO$$
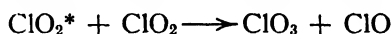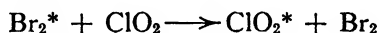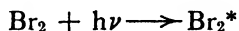
It appears to be well established that Cl_2O and Cl_2O_6 are formed in this reaction and that the Cl_2O_6 further reacts to give Cl_2O_7.

To account for these products, the reaction mechanism used to explain the corresponding gas decomposition will serve (Equations (8), (9), and (11) above). The chlorine monoxide then undergoes a bromine sensitized decomposition (22). Cl_2O_7 probably results from the photodecomposition of Cl_2O_6 (either direct or sensitized), but the mechanism of this reaction is not yet known.

To explain the low quantum yield, deactivation of the Br_2^* or of the ClO_2^* might be assumed. Since a solution of bromine in carbon tetrachloride does not fluoresce, there must be deactivation of the excited bromine either by dissociation or by small stepwise energy changes with the solvent molecules.

While the theory outlined above seems to be capable of giving a qualitative explanation of the observations, we have not yet been able to bring it into accord with the independence of the quantum yield from (ClO_2) and its dependence on light intensity. In fact, the latter seems to indicate an atomic mechanism.

The work on the photodecomposition of chlorine dioxide solutions presented in this report is interesting because it shows that there is no great difference between the decomposition (unsensitized and sensitized) in the gas and in solution. The previously supposed difference was very perplexing, because in a number of reactions carbon tetrachloride behaves as an "ideal" solvent. This study adds one more reaction to that list. Apparently the differences that do exist may be attributed to the facts that: *(a)* in the gas the Cl_2O_6 collects on the walls and is virtually removed from the reaction; in the solution it remains dissolved and undergoes further reaction; *(b)* in the gas, ClO_3 is always present and may be the carrier for chains; in solution, Cl_2O_6 is the stable form (2).

In addition, this work fits in well with the studies by Luther and Hoffmann on the thermal decomposition. Additional evidence for the existence of chlorine monoxide in insolated chlorine dioxide solutions is presented in the present report.

Further experiments are necessary to clear up the kinetics of the bromine sensitized decomposition. An investigation of the absorption and of the photodecomposition of Cl_2O_6 in carbon tetrachloride solution is needed and is being attempted.

It is hoped that by the comparative study of reactions of relatively simple substances such as chlorine dioxide, progress may be made in the understanding of sensitization and of reactions in solution.

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FORMATION OF OZONE IN AN A-C. LOW PRESSURE DISCHARGE TUBE[1]

By M. SENKUS[2]

Abstract

Passage of a glow discharge through oxygen at a pressure of 25 mm. of mercury and 17,000 volts apparently produces no ozone. The non-production of ozone is due to deozonization at the electrodes. A discharge tube is described that can be used for the demonstration and quantitative investigation of the formation of ozone in a glow discharge.

Introduction

The effects of various types of discharges through oxygen at atmospheric pressure have been described in the literature. While studying the effect of a glow discharge through oxygen at pressures of a few centimetres of mercury, some interesting results were obtained which are briefly reported here.

Experimental

Oxygen from a commercial cylinder was passed through a purifying train, and the velocity of the gas measured by a capillary type flowmeter (1). A U-shaped discharge tube (2) was blown from Pyrex glass tubing of 5 mm. inner diameter. Two larger tubes of 12 mm. inner diameter were sealed to the ends of the U-tube. Electrodes of tungsten wire were sealed into two smaller glass tubes which were connected to the 12 mm. tubes by inner seals. The length of the electrodes exposed to the gas was 14 mm. The tips of the electrodes were 15 mm. above the 12 to 5 mm. tubing seals. The inter-electrode distance was 33.5 cm. T-seals, 3.5 cm. above the upper parts of the electrodes, served as outlet and inlet for the oxygen. During all runs this tube was immersed in an ice-water bath to a point above the electrodes.

The ozonized gas from the discharge at pressures between 20 and 50 mm. was analyzed by passing it through a wash flask containing 100 cc. of 3% potassium iodide solution, and thence through a bead tower containing some of the iodide solution. The bead tower was connected through a concentrated sulphuric acid bubbler to a Cenco Hyvac pump. After regulation of the velocity and the pressure of the gas, the voltage was set at a particular value and the gas passed through the discharge for 15 min., after which the residual ozone in the tube was swept out with oxygen. The potassium iodide solution containing the liberated iodine was then acidified with sulphuric acid, and the iodine titrated with a $0.1N$ sodium thiosulphate solution, starch being used as an indicator.

The source of electrical energy was the 110 volt direct current, alternated by a 60 cycle rotary converter. The alternating current was supplied through a water rheostat to the primary of a Thordarson 25,000 volts, 1 kva, type R transformer. One side of the secondary of the transformer was grounded, while the other was connected to the electrode in the inlet arm of the discharge tube. The secondary circuit was completed by grounding the other electrode. The amperage in the secondary line was measured with a calibrated vacuum tube oscillograph.

Results

Four distinct types of discharge could be obtained with the discharge tube as the potential difference was gradually raised; a non-luminous discharge, a silent discharge, a glow current, and finally a glow discharge (Fig. 1). The type of discharge at a given voltage depends on the pressure.

Only the results obtained with the glow discharge will be described here.

The Glow Discharge

A glow discharge is characterized by a glowing column of gas that extends between the two electrodes. With extremely pure oxygen, the glowing column is greenish; a trace of nitrogen in the oxygen turns it quite yellow. Also, a thick glowing layer of light appears on the electrodes. The extent of surface of the electrodes covered with this glow is roughly proportional to the current passing through the tube.
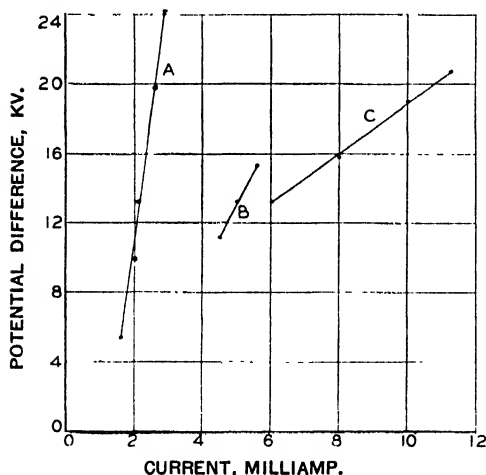
FIG. 1. *A, Silent discharge; B, glow current C, glow Discharge. Pressure, 20 mm.*

Ozonization of oxygen in the glow discharge is negligible at atmospheric pressure, apparently owing to thermal deozonization. Determinations of temperatures in the discharge at low pressures showed that far less heat was produced than at atmospheric pressure. The highest temperatures recorded in the tube (when the tube was cooled in an ice-water mixture) was 5° C., except in the immediate vicinity of the electrodes. In air, the gas in the discharge may sometimes attain a temperature of 90° C.

Several attempts were made to estimate the temperature of the electrodes. Closely adhering tin appeared to melt and fall off the electrode at voltages higher than 16,940 volts. Lead continued to adhere. This would indicate that, while the temperature of the electrodes never exceeded 300° C., a temperature of 200° C. was attained.

Ozone Formation in the Glow Discharge

For the tube set up as already described, no ozone was obtained when oxygen was subjected to either the glow current or the glow discharge.

Judging from the conditions obtaining in the tube, it was thought possible that a certain amount of ozone would be formed by the glow discharge, and would be stable in the discharge except in the immediate vicinity of the electrodes. The deozonizing action in this region is due to the high temperature of the electrodes, estimated to be well above 200° C., as well as to the presence of a high concentration of ions. Any ozone formed in the inter-electrode space would therefore be completely destroyed, since all molecules would remain for some time at the surface of, or near, the ground electrode in their passage through the tube.

To ascertain whether any ozonization took place in the inter-electrode space, the gas was pumped off from an exit in the base of the U of the tube. The discharge tube, similar in dimensions to the original one, was constructed of ordinary soft glass. The electrodes were made of platinum. Determinations were made when the gas was pumped off from an exit 4 cm. above the ground electrode, and also from an exit in the base of the U of the tube 15 cm. below the electrode. Results obtained at 25 mm. pressure and a velocity of 1.5 litres per hr. are given in Table I.

TABLE I

OZONIZATION IN THE SILENT AND GLOW DISCHARGES

Exit	Voltage	Type of discharge	Current, milliamp.	Ozone, by weight, %
Top	22,000	Silent	2.63	1.64
Bottom	22,000	Silent	2.63	1.01
Top	16,940	Glow	10.00	0.00
Bottom	16,940	Glow	10.00	0.42

Another discharge tube was constructed for the investigation of the relation between exit to electrode distance and ozone yield. The tube was made by bending a piece of glass tubing 11.8 mm. in inner diameter into a U-shape. A T-seal, 5.5 cm. above the base of the U, served as an exit for the gas. Platinum electrodes were sealed into two smaller glass tubes, which were connected to the 11.8 mm. tubing by paraffined rubber stoppers. The electrodes were thus movable.

TABLE II

EFFECT OF ELECTRODE TO EXIT DISTANCE ON THE
YIELD OF OZONE IN THE GLOW DISCHARGE

Distance from exit to electrode, cm.	Ozone, %	Yield of ozone obtained in 15 min., mg.
10	0.53	0.28
6	0.53	0.28
5	0.46	0.25
4	0.42	0.23
3	0.39	0.21
2	0.35	0.19
1	0.31	0.17
Tip above exit	0.13	0.14
Tip half way down exit	0.07	0.04
Tip below exit	0.00	0.00

NOTE:—*Voltage, 15,400; current, 7.2 milliamp.; rate of flow, 1.5 litres per hr.; pressure, 25 mm.*

The inter-electrode distance in this study was kept constant at 33 cm. The electrode connected to the high side of the transformer was always above the inlet for the gas. All runs were made at a velocity of 1.5 litres per hr. and at 25 mm. pressure. Initially the ground electrode was 10 cm. above the exit; it was gradually lowered towards and below the exit. The ozone yields at these various points are given in Table II.

Table III shows the effect of pressure on the yield of ozone in the glow discharge. The yield-pressure relation is apparently linear. Elevation of voltage similarly decreases the yield. The results are tabulated in Table IV.

TABLE III

PRESSURE-YIELD RELATION IN THE GLOW DISCHARGE

Pressure, mm. Hg.	22	25	29	32	34
Ozone, %	0.49	0.42	0.33	0.26	0.22

NOTE:—*Voltage, 19,800; current, 11.7 milliamp.; rate of flow, 1.5 litres per hr.*

TABLE IV

VOLTAGE-YIELD RELATION IN THE GLOW DISCHARGE

Voltage	8,800	9,900	11,000	12,100	13,200	14,300	15,400	16,500	17,600
Ozone, %	0.55	0.54	0.53	0.52	0.52	0.51	0.50	0.48	0.42

NOTE:—*Pressure, 25 mm. of mercury; electrode to exit distance, 10 cm.; rate of flow, 1.5 litres per hr.*

These experiments demonstrate that appreciable amounts of ozone are formed in a glow discharge in oxygen at low pressures, but that the ozone is completely destroyed by passage over one of the electrodes.

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MICROCHEMICAL TECHNIQUE

II. MODIFICATION OF THE MICROMETHOXYL APPARATUS TO THE VIEBÖCK PROCEDURE[1]

By Morris Lieff[2], Cyril Marks[3], and George F. Wright[4]

Abstract

A new absorbing chamber, which adapts the methoxyl analysis more conveniently to the Vieböck procedure, is described for the micromethoxyl apparatus. This receiver acts by hindering the gas flow so as to facilitate absorption of methyl iodide.

Although the Vieböck (5, 6) modification of Pregl's micromethoxyl determination method has been adopted by many microanalysts because of its convenience and rapidity, little change (3, 7) has been made in the apparatus. The necessity for making large numbers of methoxyl determinations in connection with the study of lignin in this laboratory has justified the re-design of Pregl's receiver. The latter, although admirably suited to the gravimetric determination of methoxyl, serves no useful purpose in Vieböck's volumetric method. Indeed, because of the slower reaction in the case of the volumetric procedures (4), a single receiver has been found to be insufficient to completely absorb the evolved methyl iodide. The double receiver used in its place is especially inconvenient when a blank on the reagents (which precaution has been found to assure more accurate and reliable results) is carried out in conjunction with the actual analysis (1).

Consequently the Pregl receiver has been replaced by an absorption tube containing four "pockets", in each of which the emerging gas bubble remains until it is displaced by the subsequent bubble. In order to insure that this displacement will always occur, the construction of these pockets requires great care. Their proper depths depend on the size of the ascending bubble, but it is essential that they be only one-half to one-third as wide as long.

This type of receiver can be adapted to the ordinary Pregl apparatus (Fig. 1) by inclining the outlet tube at an angle of about 10° from the vertical. Such a receiver is designed to contain 5 cc. of absorbent up to the bottom of the enlargement bulb, and is efficient enough to render cooling (1, 7) unnecessary. A solution of 10 cc. of 10% glacial acetic acid-potassium acetate (optically pure), containing 1 to 2 drops of bromine, is measured into a 10 cc. graduated cylinder.
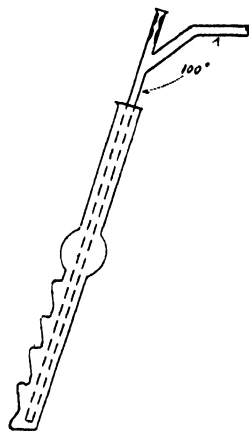
Fig. 1.

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After thorough mixing by repeatedly pouring from graduate to receiver and back, 5 cc. of absorbent is poured into the receiver, the graduate containing the remaining 5 cc. being placed close to the apparatus for the duration of the analysis. This blank is titrated in precisely the same manner as the absorbing solution. This was carried out by washing into a 125 cc. Erlenmeyer flask containing 10 cc. of 25% sodium acetate with 15 cc. of the same solution, and 5 or 6 drops of formic acid is added. After the solution is decolorized, 2 cc. of 5% potassium iodide and 30 cc. of 10% sulphuric acid are added. The $N/100$ sodium thiosulphate subsequently used for titration should be standardized by this same procedure. The blank, which varies (although not always consistently) from 0.02 to 0.30 cc. of $N/100$ thiosulphate, depending on the purity of the reagents used, is then deducted from the titer of the analysis.

A modification of this type of receiver has been incorporated into the apparatus shown in Fig. 2. Broken glass fused into the Pyrex distilling flask obviates the bumping which otherwise occurs when this thicker glass is used
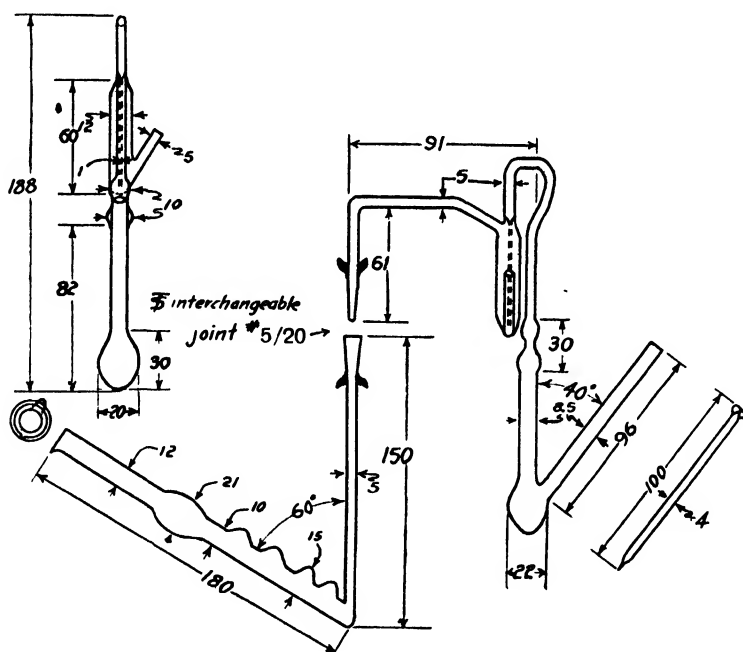
FIG. 2.   *All dimensions are in millimetres.*

in the construction. The size of the ascending gas bubble may be regulated by thickening and collapsing the walls at the apex of the angle formed by inlet tube and receiver. The ground glass joint is luted, before attachment, with a drop of acetic acid. The contents of the detached receiver are washed, after analysis, into an Erlenmeyer flask by pouring sodium acetate solution through the inlet.

When a mixture of 0.5 cc. of phenol and 2 cc. of hydriodic acid (sp. gr., 1.7) is used to decompose the sample, the apparatus works satisfactorily in a warm room, if reflux is maintained between the two bulbs of the distillation column. The analysis requires a minimum of attention to the all-important rate of gas flow when the generator recommended by Hershberg and Wellwood (2) for the micro-Dumas determination is used as a source of carbon dioxide, since no gas washing is necessary.

Acknowledgment

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STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXIX. A STUDY OF THE ACIDIC HYDROXYL GROUPS IN SPRUCE LIGNIN[1]

By R. G. D. Moore[2], George F. Wright[3], and Harold Hibbert[4]

Abstract

A demethylated spruce lignin suitable for further study has been obtained by treating methylated methanol lignin with hydriodic acid. This treatment removes the aliphatic hydroxyl, and leaves 6.9 aromatic and 0.6 carboxylic hydroxyl groups per kg. On the basis of the phenolic content it is estimated that the maximum aromatic content of spruce lignin is about 40 to 45%.

Introduction

Differentiation of the hydroxyl groups in lignin has been complicated by the presence of a multiplicity of types which are difficult to distinguish. Allocation of hydroxyl type is difficult with compounds of low' molecular weight because of the non-specificity of reagents used for this purpose, and the difficulties are magnified with a complicated substance such as lignin. In this investigation the problem has been simplified by deliberately destroying the aliphatic hydroxyl groups by a reagent (hydriodic acid) that leaves the aromatic and carboxylic hydroxyl groups unchanged.

Hydriodic acid has previously been employed for reduction of lignins (1, 4, 8), but no attempt has been made to study the reaction product, probably because of its recalcitrant nature. By demethylating a spruce lignin (OCH_3, 32.4%) (prepared from spruce wood-meal by repeated methylation with dimethyl sulphate and alkali in acetone solution, followed by hydrolysis using the methanol-hydrochloric acid method (2, 3)) by the procedure of Beckmann and co-workers (1), a product was obtained which was soluble enough in organic solvents to permit of a further investigation of its properties. It was also soluble in alkali, and contained 8.3 active hydrogen units per kg. (by the Zerewitinoff analysis in quinoline). After removal of iodine by reduction with zinc and acetic acid the product contained almost no methoxyl or halogen, was soluble in sodium hydroxide, and contained the same number (8.3) of active hydrogen units per kg. (by the Zerewitinoff analysis in quinoline).

When the substance was treated with diazomethane, 7.5 units per kg. of this active hydrogen was methylated (OCH_3, 21.0%). The remainder (8.3 − 7.5) is probably the aliphatic hydroxyl group formed by reduction, with zinc and acetic acid, of the lignin carbonyl group (0.8 group per kg.) present in spruce lignin (9). These Zerewitinoff analyses were confirmed by

(a) tosylation, and *(b)* dimethyl sulphate methylation, the latter carried out under such pH conditions that the carbomethoxyl linkages were not hydrolyzed. The methoxyl value (23.0%) accounts for all of the 8.3 active hydrogen units found in the demethylated product.

When the demethylated product is tosylated, both aliphatic and aromatic hydroxyls are replaced. Since the tosyl content is only 7.7 groups per kg., the balance, 0.6 group (8.3 − 7.7) corresponds to the residual active hydrogen content (0.8 unit per kg., Zerewitinoff analysis in quinoline), and shows that 0.5 to 0.8 hydroxyl group is present which is neither aliphatic nor aromatic. That this is carboxylic is shown by saponifying the diazomethane-methylated substance (OCH₃, 21.0%), whereby the methoxyl is decreased to 19.2% (*ca.* 0.6 group per kg.)

By subtracting this carboxyl content of 0.6 group per kg. from the total acidic hydroxyl content (7.5 per kg.) there remain 6.9 groups per kg. which must be aromatic hydroxyl, since aliphatic enolic linkages presumably would not have survived the reduction with hydriodic acid. According to Fuchs (5), alkali fusion of spruce lignin yields 5.5 parts of protocatechuic acid to one part of *p*-hydroxybenzoic acid. Application of this ratio to the 6.9 aromatic hydroxyl groups per kilogram of demethylated lignin would require about 2.9 pyrocatechol and 1.1 phenol nuclei per kg. or a maximum of about 40 to 45% of aromatic nuclei in spruce lignin.

The actual aromatic material isolated unchanged from spruce lignin has been found to contain the guaiacyl radical (6, 7). On the assumption that all the methoxyl groups are thus attached to the aromatic portion (40%), the methoxyl content of isolated lignin should be less than 12%. Most isolated spruce lignins contain 13 to 17.5% OCH₃; it is therefore probable that part of the methoxyl content in isolated lignin is non-aromatic in character.

Experimental

The methylated spruce lignin used (2, 3) contained: OCH₃, 32.4; C, 66.4; H, 6.6%.

Demethylation

A solution of 10 gm. of this lignin in 800 cc. of glacial acetic acid and 100 cc. of hydriodic acid (sp. gr. 1.7) was boiled for two hours while carbon dioxide was bubbled through the solution.

Fractionation

The solution was then concentrated to 200 cc. (18 mm.), the residue poured into dilute sodium bisulphite solution (3 litres), and the precipitate (5.5 to 6.0 gm.) removed by centrifuging. The liquors were concentrated (20 mm.) and then extracted with ether; this yielded 2.5 gm. of tarry residue, not identified. The lignin-like precipitate was dissolved in dioxane and reprecipitated by pouring the dioxane solution into 10 volumes of ether. Yield, 0.9 gm. Found: C, 63.2; H, 5.0; OCH₃, 0.7; I, 5.9%. The precipitating liquors were concentrated and poured into 10 volumes of petroleum ether

(b.p. 30° to 50° C.*). Yield of precipitate, 4.2 gm. Found: C, 63.5; H, 5.7; OCH_3, 0.7; I, 8.2%. Only methyl iodide (isolated as methyl pyridinium iodide) was found in the effluent gases.

De-iodination

The unfractionated, demethylated product was refluxed for one hour with approximately 150 times its weight of glacial acetic acid and five times its weight of zinc dust. The solution was cooled, filtered, concentrated to a small volume under reduced pressure, and the lignin precipitated by pouring into 10 volumes of water. Fractionation by the procedure outlined above yielded a dioxane-ether insoluble lignin (15%, Fraction A) and a dioxane-petroleum ether (30° to 50° C.) insoluble lignin (80%, Fraction B). Found: *(A)* C, 68.2; H, 5.4%; I, none. *(B)* C, 60.0; H, 7.0%; active hydrogen in quinoline, 8.3 per kg.

Diazomethane Methylation

Dioxane solutions of the de-iodinated products *(A)* and *(B)* were treated four times with gaseous diazomethane. Reaction product after purification showed: *(A)* OCH_3, 20.0%; *(B)* OCH_3, 21.0%. When *(B)* was boiled for nine hours with 5% ethyl alcoholic potassium hydroxide the methoxyl was decreased to 19.2%.

Dimethyl Sulphate Methylation

A sample (0.3 gm.) of diazomethane-methylated product *(B)* was acetylated for three days with pyridine (5 cc.) and acetic anhydride (2 cc.). The acetylated material was treated immediately in acetone solution (20° C.) with dimethyl sulphate (6 cc., 0.06 mole) and 30% sodium hydroxide (7 cc., 0.05 mole). After a similar re-methylation the product, dissolved in dioxane solution, was precipitated by pouring the solution into 10 volumes of petroleum ether (b.p. 30° to 50° C.); OCH_3, 23.0%.

Tosylation

It was found that the aliphatic hydroxyl group which could be methylated with dimethyl sulphate (acid conditions), but not with diazomethane, could be tosylated when 6.2 gm. of the diazomethane-methylated product (OCH_3, 21.0%) was treated in 10 cc. of pyridine with one gram of tosyl chloride for 100 hr. at 20° C. After precipitation by pouring into potassium bicarbonate solution the product was filtered off, washed with water, dried, and re-precipitated from dioxane solution by pouring into 10 volumes of petroleum ether (30° to 50° C.); OCH_3, 16.3; S, 2.9%.

When 1.5 gm. of the de-iodinated product *(B)* was tosylated twice in 55 cc. of pyridine with 6 gm. of tosyl chloride as outlined above, the product contained 11.3% sulphur (no nitrogen or halogen) and 0.8 active hydrogen per kg. (in quinoline). Calcd. for 7.7 tosyl groups per kg.: S, 11.3%.

Skellysolve F.

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THE DELIGNIFICATION OF WOOD BY STRONG ALKALINE SOLUTIONS[1]

By G. R. Lusby[2] and O. Maass[3]

Abstract

The delignification of wood by means of sodium, potassium, and lithium hydroxides has been determined with alkaline concentrations from 1.4 to 14.3 molar, and at temperatures from 120° to 180° C. A small-scale experimental technique was used by means of which the time, temperature, and concentration variables could be closely controlled.

It was found that delignification increased with concentration. A 2.9 M solution reacted about twice as fast as a 1.4 M solution of sodium hydroxide at 160° C. The difference in rate of reaction is less for solutions of concentrations of 2.9 and 4.5 M. Potassium hydroxide of 1.4 M concentration reacts only slightly more readily than sodium hydroxide of the same concentration, but the difference in reaction rate becomes more marked with increase in concentration. Lithium hydroxide reacts much more slowly than either of the other two hydroxides. There is a marked increase in reaction rate with increase in temperature. A ten degree rise in temperature somewhat more than doubles the rate of delignification. The rate of reaction is considerably diminished by the presence of sodium chloride or of reaction products in the cooking liquor.

Introduction

When wood is cooked with alkali, for the manufacture of paper-pulp, the non-cellulosic substances go into solution very rapidly at high temperatures, with the exception of the lignin, which is dissolved comparatively slowly. Because of this fact, the cooking process has been regarded in this research as the separation of lignin from cellulose. The dissolving of other wood substances is considered as incidental to the removal of lignin; that is, the main reaction is between lignin and alkali.

A preliminary study of this problem was made by Macklin and Maas (3), who investigated the rate of delignification of spruce wood by sodium hydroxide at 160° C. over the concentration range 6.2 to 14.3 molar. Their apparatus was used in the present investigation, and the technique was also the same except for a few minor changes. Studies of other problems related to the general investigation of the mechanism of alkali-cooking have been made by Richardson and Maass (4), who have measured the sorption of sodium hydroxide on cellulose; by Lusby and Maass (2), who studied the natural penetration of electrolytes into wood; and by Larocque and Maass (1), who examined the effect of the forced penetration of the liquor upon the alkaline delignification of wood.

In the present investigation, a study has been made of the influence upon the rate of delignification of (1) concentration, (2) different alkalis, (3) temperature change, and (4) neutral salts and reaction products in the cooking liquor.

Apparatus and Experimental Procedure

The apparatus and method of operation, and the analytical methods used were the same as those described by Macklin and Maass (3) in their preliminary investigation of the alkaline delignification of wood. Briefly, the experimental method consisted in cooking a 10 gm. sample of chips of black spruce wood in a small 80 cc. capacity allegheny metal digester, which was immersed in a pail of hot oil maintained at 160° C. or any other desired temperature by means of a thermoregulator.

A continuous flow of fresh liquor from a reservoir passed through the cell throughout an experiment. The rate of flow was sufficiently great that the concentration of the outgoing liquor was practically identical with the concentration of the incoming liquor. A constant pressure of about seven atmospheres was maintained inside the cell by means of a cylinder of compressed nitrogen connected through a reducing valve. At the end of an experiment the flow of liquor was stopped and the pail of oil replaced by a pail of cold water. When the cell had cooled the latter was removed, the liquor blown out of the cell by means of the nitrogen, and the cell dismantled. This experimental procedure gave an accurate control over each of the main factors governing the reaction, viz., temperature, concentration of alkali, and time.

The cooked chips were removed from the cell at the end of the experiment, placed in a dilute solution of hydrochloric acid, and disintegrated into single fibres by means of a high speed stirrer. The pulp was then washed on a Büchner funnel with water. The washed pulp was dried at 105° C. to obtain the yield of "original pulp". Duplicate samples of the pulp were then analyzed for lignin by the Ross-Potter method (5). Duplicate samples of the pulp were extracted with 1% sodium hydroxide to remove any alkali soluble lignin. The extracted pulp was then analyzed for lignin. All results were expressed as a percentage of the original bone-dry weight of the wood.

The different samples of wood used contained from 29 to 32% of lignin. In the calculation and plotting of the extent of delignification, a value of 29% was used for the lignin content of the wood, which made the results comparable with those of Macklin and Maass (3).

The sodium hydroxide used in most of the experiments was a technical grade (analysis: NaOH, 95; Na_2CO_3, 3.5; NaCl, 1.5%—on a dry basis). A 1 : 1 solution was made up and allowed to stand until the sludge settled. The clear solution was then decanted off and diluted to the desired concentration. This procedure gave a solution practically free from carbonate. No appreciable difference was noticed between the results obtained with "technical" and c.p. grades of sodium hydroxide. The potassium hydroxide was of U.S.P. quality containing 85% KOH, the impurities being carbonate and water. The lithium hydroxide was of "Merck" quality.

Experimental Results

1. *Preliminary Experiments*

Some preliminary runs in which the rate of flow of the liquor was varied indicated that diminishing the rate of liquor flow resulted in a decreased amount of changed lignin being able to diffuse outward from the chip, the extent of the delignification remaining practically the same. These results were confirmed in other runs in which it was found that wood samples cut into thin sections contained less changed lignin than thicker specimens cooked under otherwise identical conditions. Again, the same amount of delignification took place, but apparently in the thinner sections of wood the rate of diffusion of the changed or alkali-lignin was increased owing to the shorter distance that the micelles of alkali-lignin had to travel to enter the liquor. Some general conclusions may be made as a result of these and other confirmatory experiments.

(1) Variations in the volume of liquor sent through the digester cell, and small variations in the lignin content of the wood and in the wood density seemed to have no noticeable effect on the extent of the delignification, within the limits of the experimental accuracy.

(2) The chip thickness and the volume of liquor sent through the digester cell appeared to influence, by their effect on the concentration gradient of lignin in solution inside and outside the chip, the amount of changed lignin entering the liquor.

(3) The same delignification is obtained with wood of the regular chip size used in this work and with wood in very thin sections. This was expected from the rapid rate of diffusion observed by Lusby and Maass (2) on the natural penetration of sodium hydroxide into wood.

2. *The Influence of Concentration on Rate of Delignification*

The delignification data given in Table I are plotted on a time basis in Fig. 1. Concentration is seen to play an important part in the rate of reaction between sodium hydroxide and lignin. An examination of the figure indicates that a 2.9 M sodium hydroxide solution reacts with lignin about twice as fast as a 1.4 M solution. The difference in rates of reaction is not as great between 2.9 and 4.5 M sodium hydroxide. The delignification values at the end of one hour for concentrations greater than 4.5 M are somewhat higher than those found by Macklin and Maass (3). The difference may be due to the use of a different sample of wood.

3. *Cooking with Potassium and Lithium Hydroxides*

(a) *Effect of Concentration*

In Table II are given the data obtained in a series of cooks with potassium hydroxide and lithium hydroxide. The data obtained in one-hour cooks are plotted in Fig. 2. It would appear that at the lower concentrations potassium hydroxide and sodium hydroxide react with lignin at nearly the same rate;

TABLE I

Delignification with Sodium Hydroxide

Run No.	Alkali concentration, M	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignification, %
8	1.4	0.5	66.3	21.5	7.5
9	1.4	1.0	57.9	15.5	13.5
5	1.4	1.5	54.4	12.4	16.6
10	1.4	2.0	50.2	8.7	20.3
1	1.4	3.0	44.6	5.6	23.4
11	2.9	0.5	61.8	17.1	11.9
12	2.9	1.0	51.4	10.4	18.6
13	2.9	1.0	53.9	8.7	20.3
14	2.9	1.5	46.8	6.1	22.9
15	2.9	2.0	40.5	3.0	26.0
16	2.9	3.0	35.0	2.3	26.7
17	4.5	0.5	66.0	16.3	12.7
71	4.5	1.0	49.9	7.9	21.1
18	4.5	1.25	44.7	5.3	23.7
19	4.5	2.0	34.6	1.6	27.4
20	4.5	3.0	28.7	0.5	28.5
66	6.1	1.0	46.9	7.3	21.7
69	6.3	1.0	44.9	6.4	22.6
67	8.1	1.0	44.4	5.4	23.6
70	8.1	1.0	44.5	5.3	23.7
72	8.1	3.0	28.5	1.5	27.5
73	9.7	3.0	29.5	0.8	28.2
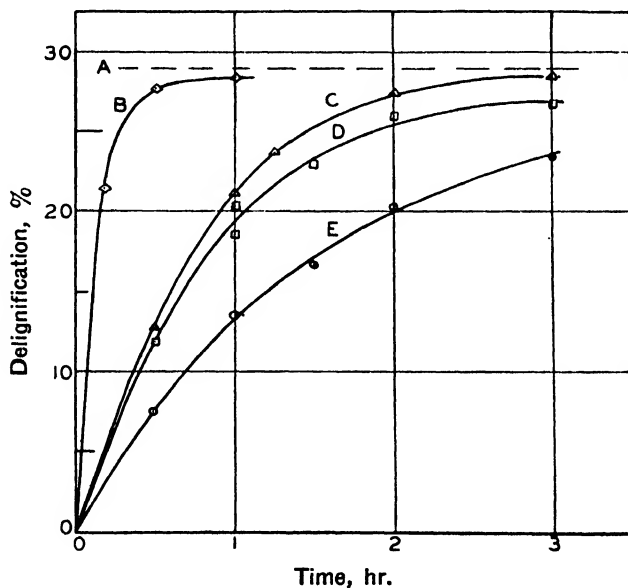
FIG. 1. *Delignification at 60° C.   A, total delignification.   B, potassium hydroxide, 14.3 M. C, D, and E, sodium hydroxide.   C, 4.5 M; D, 2.9 M; E, 1.4 M.*

but as the concentration is increased, the difference in behavior of these two hydroxides becomes more noticeable. It is evident from the figure that lithium hydroxide reacts much more slowly.

TABLE II

DELIGNIFICATION WITH POTASSIUM AND LITHIUM HYDROXIDES

Run No.	Con-centration, M	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignifi-cation, %
Potassium hydroxide					
21	1.39	1.0	60.3	15.0	14.0
22	2.90	1.5	46.5	4.6	24.4
23	2.88	1.0	50.9	8.3	20.7
24	4.56	0.5	58.5	10.1	18.9
25	4.53	1.0	44.7	4.8	24.2
26	6.26	1.0	47.4	3.4	25.6
27	9.6	1.0	46.6	1.6	27.4
31	14.3	0.17	53.1	7.5	21.5
32	14.3	0.50	43.9	1.2	27.8
28	14.2	1.0	42.1	0.6	28.4
Lithium hydroxide					
29	1.38	1.0	59.4	17.2	11.8
30	2.89	1.0	62.7	15.4	13.6
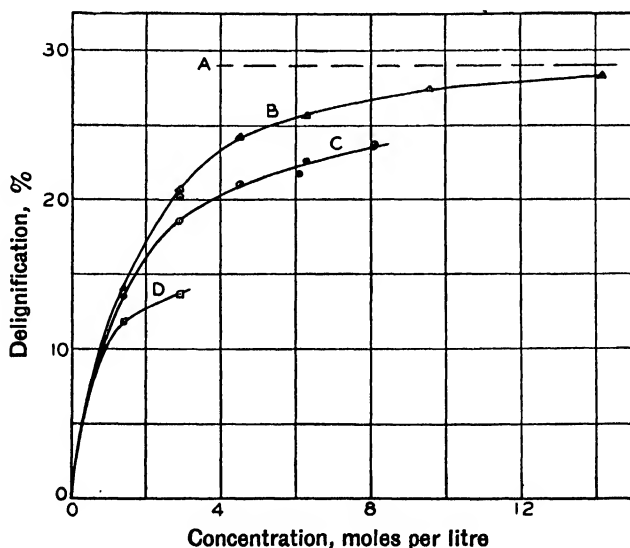
FIG. 2. *Delignification in one-hour cooks with sodium, potassium, and lithium hydroxides. Temperature, 160° C. A, total delignification. B, potassium hydroxide; C, sodium hydroxide; D, lithium hydroxide.*

(b) Effect of Time on Delignification

The shape of the delignification–time curve for the 14.3 M potassium hydroxide is shown in Fig. 1. For the 10 min. run the chips were cut into thin sections similar to planings, to permit as rapid penetration as possible of the liquor into the wood. This is an important consideration when the cooking time is only 10 min.

4. *Effect of Temperature on Delignification Rate*

Runs were made with sodium and potassium hydroxides of different concentrations at 120°, 140°, and 180° C. The data obtained are given in Table III. It is to be observed that there is a marked increase in the delignification with rise in temperature, the rate approximately doubling with a 10 degree rise in temperature. The significance of these results will be fully discussed in a subsequent paper.

TABLE III

THE INFLUENCE OF TEMPERATURE

Run No.	Con-centration, M	Temp., ° C.	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignifi-cation, %
Reagent—Sodium hydroxide						
33	2.9	140	1.0	66.5	23.2	5.8
34	2.9	180	1.0	17.0	0.4	28.6
35	14.3	120	1.0	78.2	24.1	4.9
36	14.3	140	1.0	59.1	11.7	17.3
37	14.3	140	3.0	36.4	1 2	27.8
Reagent—Potassium hydroxide						
38	14.3	120	1.0	70.3	23.6	5.4
39	14.3	140	1.0	52.6	4.6	24.4

5. *The Influence of Sodium Chloride in the Cooking Liquor on the Rate of Delignification*

The effect of added sodium chloride in the cooking liquor on the rate of delignification can be seen in Table IV. The cooking liquor was made up by adding a definite amount of sodium chloride to 2.9 M sodium hydroxide.

TABLE IV

THE INFLUENCE OF SODIUM CHLORIDE ON THE RATE OF DELIGNIFICATION

Run No.	Reagent	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignifi-cation, %
42	2.97 M NaOH 4.26 M NaCl	1.5	61.1	12.9	16.1
43	2.97 M NaOH 4.26 M NaCl	3.0	47.1	6.4	22.6
14	2.90 M NaOH	1.5	46.8	6.1	22.9
16	2.90 M NaOH	3.0	35.0	. 2.3	26.7

Since the increase in volume accompanying the dissolving of this salt decreased the molar concentration of the alkali, the final concentration was adjusted to give the same molar concentration of sodium hydroxide as the liquor to which no sodium hydroxide was added.

The addition of 4.26 moles of sodium chloride to a 2.9 M solution of sodium hydroxide decreases the rate of reaction to about one-half its value when this salt is absent. This decreased activity of the sodium hydroxide in the presence of the chloride is to be ascribed to a common-ion effect taking place; this depresses to some extent the dissociation of the sodium hydroxide.

6. *The Influence of Reaction Products on the Rate of Reaction*

Some experiments were carried out in order to study the influence of the reaction products on the rate of the delignification reaction. The results obtained are set forth in Table V, along with the mean of two control experiments.

TABLE V

THE INFLUENCE OF THE REACTION PRODUCTS ON THE RATE OF DELIGNIFICATION AND OF
MERCERIZATION IN STRONG ALKALI

Run No.	Reagent	Time, hr.	Yield of extracted pulp, %	Lignin in extracted pulp, %	Delignification, %
12, 13	2.90 M NaOH	1.0	52.7	9.6	19.4
46	2.90 M NaOH [1]	1.0	61.3	15.6	13.4
47	2.90 M NaOH [2]	1.0	56.0	13.3	15.7
48	2.90 M NaOH [3]	1.0	60.1	14.2	14.8
50	2.90 M NaOH [4]	1.0	50.4	9.1	19.9

NOTE.—[1] *52 gm. per litre of redissolved alkali-lignin added.*
[2] *Waste-liquor containing 38 gm. per litre alkali-lignin.*
[3] *100 gm. per litre of cellulose decomposition products.*
[4] *Mercerized for eight hours in 14 M NaOH.*

In the first experiment, Run 46, the cooking liquor contained 52 gm. per litre of redissolved alkali-lignin, prepared by triturating the required amount of dry alkali-lignin in a mortar with 2.90 M sodium hydroxide solution. Sufficient fresh alkali was then added to this solution to restore the concentration to the original value of 2.90 M. It was realized that in this first experiment, the redissolved alkali-lignin might not have the same action as alkali-lignin which goes into solution during the cooking process. In a second experiment, Run 47, a waste liquor freshly obtained from a previous soda-cook was used, containing 38 gm. per litre of alkali-lignin, and of 2.90 M concentration with respect to sodium hydroxide, as determined by titration.

In a third experiment, Run 48, the liquor contained 100 gm. per litre of cellulose decomposition products. These decomposition products were obtained by heating 200 gm. of bleached soda-pulp at 180° C. for one hour in 1800 cc. of 2.90 M sodium hydroxide. At the end of this time, 85% of

the soda-pulp had dissolved to give a dark reddish-brown liquor. The alkalinity of this liquor was built up to 2.90 M and the liquor used in the cooking experiments reported in Table V.

A consideration of the results of this table indicates that the presence either of alkali-lignin, or of cellulose decomposition products in the cooking liquor, markedly decreases the rate of reaction. It is to be noticed that the presence of the alkali-lignin seems to have a more pronounced effect than the same amount of cellulose decomposition products. Both the alkali-lignin and the cellulose decomposition products are known to exist in the liquor as colloids, which absorb alkali. It is therefore likely that this decrease in the rate of delignification is due to a decrease in the effective alkali concentration due to the loss of sodium hydroxide by sorption by these colloids. This lower effective concentration of alkali would not be apparent on titration, because the adsorbed alkali would return to the solution as neutralization took place.

7. The Influence of Swelling on the Rate of Reaction

It was thought that the increased rate of reaction that is observed at the higher alkali concentrations might in part be due to a change taking place in the molecular arrangement of the lignin particles, brought about at the same time as the swelling of the cellulose which occurs as the result of the sorption of alkali at high concentrations of sodium hydroxide. In one experiment (Run 50, Table V), wood chips were allowed to stand for eight hours at room temperature in absorption equilibrium with 14 M alkali, after which most of the alkali was removed with water. Subsequent cooking with 2.90 M alkali gave the same residual lignin content as the control experiment. This indicates that pretreatment involving swelling of the cellulose has no influence on the rate of subsequent delignification. The increased activity at higher alkali concentrations would seem to be a specific property of the more concentrated solutions.

Discussion

The results of the experiments with 1.4, 2.9, and 4.5 M sodium hydroxide solutions are not directly comparable with the results that would be obtained with liquors of the same composition under commercial conditions, since it has been shown that the presence of reaction products considerably slows up the cooking reaction. They may be compared in a relative way, however, and give an accurate indication of the influence that concentration plays in the alkaline-delignification reaction. In commercial pulping practice, it has been commonly observed that the addition of "black liquor" to the cooking liquor increases the bleach requirement of the pulp. It may be that the increased quantity of reaction products in the liquor caused this effect by decreasing the extent of the cooking.

Ross (5) found that pulp of commercial quality could be made by cooking wood with 14 M sodium hydroxide solution, and the same should be true of cooking with 14 M potassium hydroxide solutions. The much greater rapidity

of cooking which obtains in the case of potassium hydroxide would depend upon the efficiency of the recovery system and the desirability of the pulp in regard to its physical and chemical properties.

From the investigation of the rates of reaction of lithium, sodium, and potassium hydroxides with lignin in wood, the generalization may be made that the rate of reaction increases with the atomic weight of the alkali metal. Rubidium and caesium hydroxides would be expected to react with lignin even faster than does potassium hydroxide. In a subsequent paper an attempt will be made towards elucidating the mechanism of the lignin-alkali reaction, by comparing the rates of reaction obtained with different alkalis with data on viscosity, activity, absorption, etc., of the alkali solutions employed.

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Section B

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SECTION B

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Subjects

ERRATUM

Page 354, second paragraph, line 13, for "100 cc." read "50 cc."